LIFE CYCLE ANALYSIS OF ALFALFA STEM-BASED BIOETHANOL PRODUCTION SYSTEM

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ABSTRACT

Alfalfa stem can be a potential feedstock for producing bioethanol. Numerous studies have been carried out to assess the conversion of different feedstocks into bioethanol, although studies related to life cycle assessment (LCA) of feedstocks such as alfalfa are limited. However, LCA does serve to highlight areas where positive and negative impacts can be expected in the overall biomass to ethanol process. This research therefore focuses on investigating and evaluating an alfalfa bioethanol production system in terms of five key life cycle impact categories: abiotic depletion (AD), acidification (A), eutrophication (E), global warming (GW), human toxicity (HT), and energy demand. The study concerns three subsystems: the cultivation subsystem (S1), the baling and pre-processing subsystem (S2), and the ethanol conversion subsystem (S3). Each subsystem could have different scenarios depending on specified input combinations, and SimaPro 7.2 with CML 2 baseline 1990 V2.05 version was used to assess environmental impacts.

The results of energy assessment correspond to LCA results, showing that the environmental impact associated with alfalfa-ethanol production increases with increased energy demand. Energy analysis of S1 showed that the energy requirements for producing 1 kg of alfalfa under non-irrigated and irrigated cultivation were between 0.63 MJ to 1.30 MJ and 0.51 MJ to 0.94 MJ, respectively. The best input combination in S1 was inorganic fertilizer with irrigation, for it consumed 0.51 MJ/kg energy and resulted in the least environmental impact. The energy requirements for the postharvest pre-processing of 1 kg of alfalfa biomass were 0.82 MJ to 1.62 MJ under different

scenarios, with the drum drying requiring the highest energy in S2: 0.197 MJ of electricity and heat per hectare.

Considering the three systems (namely S1, S2, and S3) demonstrates that irrigated alfalfa production scenarios revealed lower energy demands in comparison to non-irrigated scenarios; inorganic scenarios showed lower energy demand over organic scenarios. Compared to the use of organic fertilizers, application of inorganic fertilizers has decreased the impact with respect to AD, A, GW, and HT while slightly increasing E in S1, S2, and S3. Therefore, the most favourable scenario was the inorganic irrigated scenario in all subsystems. The LCA results concluded that GW was the most influential impact category for all three subsystems, whereas AD, A, E, and HT had a comparatively lower impact on each system.

To produce 1 L of ethanol, 32.78 MJ (minimum) to 38.43 MJ (maximum) of energy input was required for S3 in all production scenarios at 50% water recycling. In S1, S2, and S3, the inorganic irrigated scenarios had lower energy demands than the organic irrigated scenarios. The highest energy consuming process in S3 was ethanol plant heat energy. Overall, the inorganic, irrigated, and 50% water recycling represented the best case scenario for all subsystems (S1, S2, and S3) in terms of energy demand with an average of 7.82 MJ for 1 kg of alfalfa biomass input. Comparing the three subsystems shows that the alfalfa cultivation subsystem (S1) consumed 6.2% to 15.1% of the total energy. The ethanol conversion subsystem (S3) is the highest energy consuming subsystem in this study, falling into the 77.5% - 94.8% range of the total for different scenarios. The baling and pre-processing subsystem (S2) required between 3.5% and

4.0% of the total energy. Future studies could assess different allocation methods and co-product credits for the establishment of a sustainable cellulosic biorefinery.

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LIST OF ACRONYMS AND ABBREVIATIONS

A	Acidification
AD	Abiotic depletion
CML	Centre of Environmental Science
CO_2	Carbon dioxide
CH_4	Methane
E	Eutrophication
FPU	Filter paper unit
FU	Functional unit
GHG	Greenhouse gas
GJ	Giga joule
GW	Global warming
HT	Human toxicity
ISO	International Organization for Standardization
K_2O	Potassium fertilizer
LCA	Life cycle analysis/assessment
LCI	Life cycle inventory
LCIA	Life cycle impact assessment
P_2O_5	Phosphorous fertilizer
MJ	Mega joule
MW	Megawatt
S1	Subsystem 1: alfalfa cultivation subsystem

S2	Subsystem 2: baling and pre-processing subsystem
S3	Subsystem 3: ethanol production subsystem
Sb	Antimony
SHF	Separate hydrolysis and fermentation
SSF	Simultaneous saccharification and fermentation

1. Introduction

The ethanol industry is rapidly expanding around the world (Worldwatch Institute 2006), and average growth in the global ethanol market has been 10.9% since 2001 (Dunnette et al. 2008). It is reported that world ethanol production in 2005 was approximately 46 billion litres per year with an anticipated growth of 76 billion litres per year by 2010. The United States and Brazil are the main producers, supplying 49.96 billion and 26.19 billion litres of ethanol respectively in 2010; Canada produced only 237 million litres in 2007, growing to 352 million litres by 2010 (Renewable Fuels Association 2010). However, Canada's commitment to climate change and related biofuel mandates are driving interests for the accelerated development of a Canadian ethanol industry.

1.1 Significance of the study

Ethanol has been used as a transportation fuel in a number of countries and has been deemed as a partial substitute for gasoline (Garcia et al. 2009b, 2010a, 2010b; Kaylen et al. 2000; Spatari et al. 2005; Kadam 2002; Schmer et al. 2008; Mabee and Saddler 2010). Ethanol from lignocellulosic feedstock (the lignocellulosic residue from primary harvest) has become a crucial and debatable topic. The term "lignocellulosics" is applied to materials composed mainly of cellulose, hemicellulose, and lignin (Dale 1983; Fang et al. 2010), and their composition varies significantly by crop, agronomic conditions, and other factors. The composition of cereal straw is approximately 15%-30% hemicellulose, 35%-50% cellulose, and the rest is primarily lignin, less extractive and ash (Wyman 1994; Propheter 2009; Knauf and Moniruzzaman 2004; Mabee and Saddler 2010). Because of the diversity in feedstock chemical composition, potential yields of ethanol vary significantly among substrates and the conversion technologies being used (Mabee and Saddler 2010). Materials such as agricultural residues (corn stover, canola straw, sugarcane bagasse), herbaceous crops (alfalfa, switchgrass), short rotation woody crops (poplar, willow), forestry residues, wastepaper, and other wastes (Kim and Dale 2004; Wyman 1994) are included into the category of lignocellulosic biomass. Availability and low cost are key drivers in the selection of biomass for biofuel production (Onuki et al. 2008). Ethanol from grain has been criticized for its unfavourable net energy balance and significant arable land and water requirements, as well as environmental impacts such as soil erosion, loss of biodiversity, higher volatile organic compounds, and N_2O pollution (Solomon et al. 2007). Thus, bioethanol derived from biomass is recognized as an appropriate substitute for transportation fuel.

Legislation to limit greenhouse gas (GHG) emissions is a key driver of lignocellulosic ethanol (Mabee and Saddler 2010) which aims to reduce GHG emissions drastically. In Canada, the use of bioethanol is being considered as one of the important measures to address the climate change commitment (Mabee and Saddler 2010; Farrell et al. 2006; MacLean et al. 2000). Related factors include declining oil reserves, economic volatility, and insecurity caused by rising gasoline prices (Vadas et al. 2008). The production and use of renewable fuels manufactured from lignocellulosic agricultural feedstocks, such as alfalfa and other agricultural residues, represents an opportunity to reduce GHG emissions; the process could offer a synergistic benefit to both the agricultural and transportation sectors. Several technologies have been developed during the past 80 years that allow this conversion process to occur, and the clear objective now is to make this process cost-competitive in today's markets. The key advantages of lignocellulose-based ethanol versus grain-based ethanol are access to a wider array of feedstocks, avoidance of conflicts with land use for food crops, a much greater displacement of fossil energy per litre of ethanol, and the drastic reduction of net GHG emissions (IEA 2004). Moreover, the recent surge in demand for grain had an impact on other sectors which rely on this energy source. The food versus fuel debate also encourages lignocellulosic feedstocks (Wyman 1994). Kadam (2002) also noted that agricultural residues, forestry residues, pulp and paper waste streams, and municipal solid waste are abundant and underutilised resources available for ethanol conversion. Some studies, though, have demonstrated that removing agricultural waste such as stalks and leaves has negative effects on soil, the environment, and future crops. However, cellulosic biomass can be produced on marginal lands with less or no inputs and minimal effect on the environment. In fact, lignocellulosic biomass increases the production capacity of biofuel while minimizing its negative social and environmental impacts (Slade et al. 2009). In the Midwestern United States and Brazil, for example, ethanol production technology from corn or molasses is already well established (Kadam 2002).

Major ethanol producers such as, the United States have identified agricultural and forestry residues, municipal solid wastes, and herbaceous and woody crops as feedstock for ethanol production. In Canada, ethanol production is still grain-based and dominated by wheat and corn. Canada's ethanol production, however, makes only a small contribution (0.24 billion litres/year production capacity) to the international ethanol market. Canada's grain-based ethanol production accounts for 92% of total ethanol production capacity (Olar et al. 2004). Motivated by a positive policy environment, Canada's ethanol industry is thriving with significant expansion of existing plants and projected biorefineries. In particular, there is emerging interest in lignocellulose-based ethanol production in Canada. For instance, Ottawa-based Iogen Corporation successfully operates demonstration cellulosic ethanol plant using wheat straw, while Greenfield Ethanol in Chatham, Ontario has developed a pilot plant using corn cobs as feedstock (Mabee and Saddler 2010). Meanwhile, the available and emerging ethanol plants in Western Canada exhibit great potential for ethanol production from lignocellulosic feedstock. Alfalfa has been targeted as a potential lignocellulosic feedstock, with agronomic and breeding studies underway to optimize this legume for biorefinery applications (Margie Gruber, Deputy Leader, Canadian Cellulosic Biofuels Network, Personal Communication). The majority of alfalfa crop area is found in the three Canadian prairie provinces (Saskatchewan, Alberta, and Manitoba), with a total of 3.39 million hectares (Statistics Canada 2001). In Saskatchewan, approximately 1.6 million hectares is under alfalfa or alfalfa mixture (mixtures with grasses or other hay crops) cultivation and approximately 1.0×10^6 tonnes or 23×10^3 hectares land base is utilized in the forage processing industries, namely alfalfa pellets, cubes, and hay densification (Saskatchewan Ministry of Agriculture 2010c).

Although numerous studies have been undertaken to assess the conversion of feedstock into ethanol, very few studies focus on energy and environmental impacts (Blottnitz and Curran 2007). Frequently, policy and decision makers agree that the environmental costs and benefits of energy from biomass need to be better understood. One approach that can be used to identify and quantify costs and benefits of biomass energy production is life cycle assessment (LCA). There have been techno-economic studies done by the Agriculture and Agri-Food Canada (2002) using the AAFC ethanol model for existing plants in southern Ontario region. However, no life cycle analysis has been done for alfalfa stem-based bioethanol system in Canada to date.

In the broadest sense, LCA is defined as a holistic tool for the systematic evaluation of environmental aspects of a product or service system through all stages of its life cycle (Blottnitz and Curran 2007; Burgess and Brenan 2001). It is an analytical tool for quantifying emissions, resource consumption, and energy use associated with a product or process (Mann and Spath 1997; Consoli et al. 1993). According to Garcia et al. (2009a), LCA enables the evaluation of environmental burdens associated with a product and identification of opportunities for environmental improvements. However, LCA is dependent on the data gained from any given scenario. A thorough LCA is required to provide information about process sustainability and viability. It is difficult to draw conclusions regarding the precise quantitative energy and the environmental benefits or costs of any particular biofuel pathway without detailed case-specific information and analysis (Cherubini et al. 2009). Employing LCA helps to highlight areas where positive and negative impacts can be expected. The unsolved challenges related to process efficiency, sustainability, and the industry viability at the commercial level necessitates more research on cellulosic ethanol production specifically based on alfalfa stem biomass. The actual production of a fuel such as ethanol can vary significantly depending not only on the feedstocks, but also on the location (Cherubini et al. 2009). To address the potential overall benefits, it is important to perform an analysis of the entire life cycle of the process. This study aims to assess the life cycle for ethanol production using alfalfa stem biomass.

1.2 Objectives

The main goal of this thesis is to study the life cycle of alfalfa stem-based bioethanol production system from alfalfa cultivation, processing, and transportation up to ethanol conversion. The specific objectives of this study are:

1. to investigate alfalfa cultivation, logistics, and processing in terms of input use and energy consumption;
2. to calculate the mass balance of bioethanol conversion process using steam explosion pre-treatment and simultaneous saccharification and fermentation technology; and
3. to evaluate the alfalfa bioethanol production system in terms of five environmental impacts categories, which are abiotic depletion (AD), acidification (A), eutrophication (E), global warming (GW), and human toxicity (HT).

The five environmental impact categories in LCA, that need to be elaborated here in order to provide a better understanding of the methodological approach used in this study. They include the following:

1. Abiotic depletion (AD): It refers to the "decrease of the unique natural configurations of elements in resources in the environment or the decrease availability of the total reserve of potential functions of resources" (Guinee et al. 2001). It encompasses both the use of renewable and non-renewable resources.

2. Acidification (A): This is caused by acids and compounds which can be converted into acids. The most significant man-made sources of acidification are combustion processes in electricity and heating production, and in transportation (LCA Food 2003).
3. Eutrophication (E): This is also termed as “ nutrient enrichment," "nutrification" and "oxygen depletion". Substances under this category are emitted both to the atmosphere and to water (Finnveden and Potting 1999). Emissions of nitrogen, phosphorous, and organic materials are some of the major substances associated with this impact category.
4. Global warming (GW): This expression refers atmospheric warming results in climate change. One of the major contributors to global warming is the combustion of fossil fuels such as oil, coal, and natural gas (LCA Food 2003). The main greenhouse gases are carbon dioxide (CO_2), nitrous oxide (N_2O), and methane (CH_4). Global warming is generally defined in terms of CO_2 equivalents so that there is a common reference point for quantifying and comparing the severity of the impact of each greenhouse gas. This measure is well articulated by the Intergovernmental Panel on Climate Change (IPCC 2007). Carbon dioxide equivalents are basically a method used to measure the effect of various greenhouse gases. In other words, the various green house gases are converted into CO_2 equivalents so that there is a common reference point for quantifying and comparing the severity of the impact of each greenhouse gas. In this case, one CO_2 equivalent is equivalent to the effect of the emission of 1 kg of CO_2. For instance, over a period of 100 years, CH_4 has a global warming potential of 25

while N_2O has 298. To be precise, 1 million metric tonnes of CH_4 emissions are equivalent to 25 million metric tonnes of CO_2 while 1 million metric tonnes of N_2O emissions generate an equivalent 298 million metric tonnes of CO_2.

5. Human toxicity (HT): This impact category characterizes toxic chemicals with relevance to human exposure. It can be measured by using threshold limits on human toxicity and is defined as equivalent to 1,4-DB (dichloro butanic acid).

1.3 Organization of the thesis

This thesis is organized into five chapters: Introduction, Literature Review, Methodology, Results and Discussion, and Conclusions and Recommendations for future research. Literature related to this thesis is reviewed in chapter 2, based on literature related to alfalfa production, processing, and life cycle analysis of different lignocellulosic feedstocks. The review provides information on the current status of alfalfa cultivation in Canada and the biological, physiological, and agronomic aspects of the crop. A description of the ethanol conversion technology adopted in this study is also provided along with a thorough literature survey of LCA studies on lignocellulose based ethanol made from various feedstocks and intended for use as a transportation fuel. Furthermore, chapter 2 discusses the mechanism and method of LCA with its application to the assessment of bioethanol production, assumptions used, and findings obtained. Chapter 3 summarizes materials and research methodology including data acquisition, assumptions, software used, and the method of analysis. The methodology has been designed to achieve specific objectives with a cradle-to-gate LCA. The depth and width of any life cycle analysis is based on its system boundary. In this study, the system consists of three major subsystems, namely: i) alfalfa cultivation; ii) baling and pre-processing; and iii) ethanol production. Data are gathered accordingly for the requirements of each subsystem and input use, and then incorporated with justifiable assumptions. The results are presented and discussed in chapter 4. Chapter 5 provides a summary, conclusions, and recommendations for future research. The complete mass balance sheet, inventory data, and some detailed analyses are given in the Appendix.

2. Literature Review

This section consists of three parts. It includes concise information on agronomic aspects and logistics of alfalfa, ethanol production technology (pretreatment, hydrolysis and fermentation and distillation), concepts, and related studies on life cycle analysis.

2.1 Alfalfa as biomass

Alfalfa is the predominant source of high quality feed for horses, dairy cows, and other livestock. It serves as high protein roughage in pasture and hay mixtures for livestock. In Canada's processed forage industry, it is regarded as the "queen" of forages (Wu 2004; Government of Alberta 2004). Alfalfa has the potential to be a dual-purpose crop; that is, the stems would be harvested for fuel and the leaves for feed and other products (Rock et al. 2009; Dale 1983; DeLong 1995; Downing et al. 2005; Anderson et al. 2008). Allocation procedures are often used in analysing dual-purpose crops like alfalfa. In other words, allocation involves partitioning of input-output flows of a unit process to a feedstock in terms of mass or energy. For alfalfa, the mass allocation is based on the fact that the legume produces leaves and stems in equal proportions; however, the parts differ in terms of protein content allocation (28.5% for leaves and 10.5% for stems on dry basis). Table 2.1 presents alfalfa allocation coefficients based on a study by Garcia et al. (2010b). Canada is a major exporter of alfalfa seed originating from Alberta, Saskatchewan, and Manitoba. Table 2.2 presents hectares under alfalfa cultivation in Canada, clearly demonstrating the dominance of the prairie provinces as major alfalfa producers (Statistics Canada 2001).

Table 2.1: Partitioning fraction of mass and protein based allocation, reported by Garcia et al. (2010b).

Allocation method	Allocation	
	Leaves (%)	Stems (%)
Protein content	73.1	26.9
Mass	50.0	50.0

Table 2.2: Alfalfa or alfalfa mixture cultivation area, adapted from Statistics Canada (2001).

Region	Area under cultivation ('000 ha)
Atlantic	37
Quebec	235
Ontario	652
Prairie provinces	3385
British Columbia	196

The majority of alfalfa cultivation in Canada comprises mixtures (more than 80% of seeded area). In eastern Canada, the grass grown with alfalfa in mixtures is mainly timothy (*Phleum pratense*). A higher percentage of alfalfa (perhaps 50%) is grown in pure stands in eastern Canada. In the prairies, the major grass mixed with alfalfa is smooth bromegrass (*Bromus inermis*) or meadow bromegrass (*Bromus riparius*). In dryer regions of the prairies, alfalfa is normally mixed with crested wheatgrass (*Agropyton cristatum*). Overall, most of the alfalfa on the prairies is seeded in mixtures while in British Columbia, most of the alfalfa is grown in pure stands (Coulman, B., Professor, Department of Plant Sciences, University of Saskatchewan, Personal Communication). Table 2.3 depicts the recommended seeding rates of alfalfa in Saskatchewan soil zones. The seeding rates can be varied depending on the quality of seeds, cropping pattern, seeding conditions, and the end use of the crop (Saskatchewan Forage Council 2008).

Table 2.3: Recommended seeding rates for Saskatchewan soil zones, adapted from Saskatchewan Ministry of Agriculture (2010a).

Soil zone	Seeding rate (kg/ha)
Brown	4.5
Dark brown	9.0
Black and grey	9.0
Irrigation	9.0

As the world's largest alfalfa seed producing region, Canada and the United States together produce over 50 million kilograms of alfalfa seed in a normal year (Government of Alberta 2004). Alfalfa is native to the Middle East and can be grown from very cold northern plains to high mountain valleys, as well as from rich temperate agricultural regions to Mediterranean climates (Anderson et al. 2008). Infrastructure requirements (such as cultivation, harvesting, and storing technologies) are well established for this crop in United States (Anderson et al. 2008).

Alfalfa enriches the soil by fixing nitrogen, paving the way for grasses and shrubs to thrive and even dominate the landscape. After harvest, significantly more nitrogen is left in the residue of a forage legume compared to that of a non-legume annual crop. It is observed that alfalfa produces adequate yields under less than optimum soil moisture or nitrogen fertility by using its deep rooting system and nitrogen (N) fixing bacterium (Anderson et al. 2008). The symbiotic nitrogen fixation of alfalfa is around 114-300 kg/ha. For an un-harvested forage legume, which is incorporated as green manure, it is estimated that about 65% of the nitrogen fixed by the legume crop becomes available over the next several growing seasons. Fertilizer replacement values of up to 150 kg N/ha following forage legumes in rotation has been reported. Alfalfa hay crops remove approximately 45 kg N/t of forage (85% dry matter basis) annually. The crop thrives in well-drained fertile soil with plenty of rainfall, but breeding efforts have developed varieties that are winter hardy, pest resistant, and more heat and drought tolerant.

Mineralization rates of green manures are expected to be slightly higher due to greater nitrogen content of the younger tissue. In Winnipeg and Portage la Prairie, Manitoba, studies determined that nitrogen fixation rates of alfalfa increased from 174 kg/ha in year one to 466 kg/ha in the third year of the stand; the net soil nitrogen balance increased from 84 kg/ha to 137 kg/ha from year one to three (Saskatchewan Forage Council 2008).

Fertilizer application rates vary among geographical locations. For the western Canadian context, the amount required as per literature is given in Table 2.4. Rive (1914) has noted that 13.61 kg nitrate of soda, 136.18 kg bone-meal, and 22.68 kg muriate of potash can replace the amount of nutrient removed from a given alfalfa yield. Garcia et al. (2010a) reported 36.2 kg of N, 103.2 kg of K_2O, and 101.4 kg P_2O_5 per hectare of fertilizer usage in their study on alfalfa based ethanol production. Table 2.5 provides information on nutrient removal from eight tonnes of alfalfa yield.

Table 2.4: Application of fertilizer for alfalfa cultivation.

Fertilizer	Amount (kg/ha)	Reference
Nitrogen	3.67	Saskatchewan Ministry of Agriculture 2010a
Phosphorous	36.71	Saskatchewan Ministry of Agriculture 2010c
Potasium	27.54	Government of Alberta 2010
Sulfur	5.51	Government of Alberta 2010
Manure	4046.00	Government of Alberta 2010

Table 2.5: Nutrient removal of alfalfa (for eight tonnes of alfalfa yield), reported by Sahota (2007).

Nutrient	Amount (kg)
Nitrogen (N)	204.12
Phosphorous (P_2O_5)	54.43
Potassium (K_2O)	217.72
Magnesium (Mg)	18.14
Sulfur (S)	18.14

The yield that may reasonably be expected from alfalfa will depend upon locality, season, and variety used. Approximately 40 tonnes of green fodder per hectare, or 4 tonnes of hay, should at least be secured when the field is well-established. The average yield has been reported as approximately 50 tonnes of green fodder per hectare or 15 tonnes of hay over eight years at the Oregon Agricultural Station (Rive 1914). Table 2.6 depicts average yields of a few alfalfa varieties grown in Saskatchewan.

Table 2.6: Yield (kg/ha in dry basis) of alfalfa varieties in Saskatchewan by soil zone (1992 - 1996), adapted from Saskatchewan Ministry of Agriculture (2010b).

Variety	Soil Zone			
	Brown	Dark Brown	Black/Gray	Irrigation
Heinrichs	3584	6930	6343	10780
Rambler	3626	6580	6280	9790
Rangelander	3914	6510	6531	10230
Apica	4367	7070	6217	11000
OAC Minto	3955	6930	6468	10890
Algonquin	4038	6650	6343	10670
Anchor	3832	7070	6092	11440
Alouette	3955	7210	6217	-
Barrier	3626	6860	6154	11770
Vernal	3955	6300	6154	11000
Profit	3955	7280	5652	-
Beaver	4120	7000	6280	11000

Harvesting (cutting) of alfalfa is carried out using a mower conditioner (Tsatsarelis and Koundouras 1994; Agriculture and Natural Resources 2005). Table 2.7 and Table 2.8 provide literature data for agricultural machinery usage. In Table 2.7, figures for agricultural machinery employed in different tasks were presented as per Gallego et al. (2007) from their study in Spain. Both Table 2.7 and Table 2.8 summarize field operations consisting of ploughing (with chisel subsoiler), levelling (disk harrow), seeding (cereal seeder), fertilizer, pesticide and herbicide application (tractor; fertilizer spreader and sprayer), and harvesting (mower conditioner).

Table 2.7: Data on tractor use in different tasks for 1 ha of alfalfa/ life cycle for field preparation, reported by Gallego et al. (2007).

Equipment	Task	Tractor power (hp)	Diesel (L/FU*)	Speed (h/ha)	Oil (L/FU)
Tractor (chisel-subsolier)	Deep ploughing	100	20	1	0.25
Tractor (disc harrow)	Levels out the soil and prevent it from getting flooded	72	14.4	1	0.25
Tractor (roller)	Levels out the soil and prevent it from getting flooded	100	5	0.25	0.06
Tractor (field sprayer herbicide 600 l)		60	12	1	0.25
Tractor (fertilizer spreader centrifugal)	Fertilizing	60	3.6	0.3	0.25
Tractor (rotary harrow)		100	7	0.35	0.25
Tractor (cereal seeder)	Seeding	100	14	0.7	0.25

*The functional unit (FU) selected is 1 ha of alfalfa/cycle. On average, one cycle equals 4.5 years. Diesel and oil are given as litres per functional unit (L/FU).

Table 2.8: Machinery used for maintenance to harvesting of 1 ha of alfalfa/ life cycle, reported by Gallego et al. (2007).

Machinery	Tractor power (hp)	Diesel (L/FU*)	Speed (h/ha)	Oil (L/FU)
Tractor (harvester, 7 cuts/year)	72	129.6	2	2.25
Tractor (windrower, 7 times/year)	72	64.8	1	1.13
Tractor (field sprayer insecticide 600 l)	60	54	1	1.13
Tractor (field sprayer herbicide 600 l)	60	54	1	1.13
Tractor (fertilizer spreader)	60	16.2	0.3	0.34
Tractor (vacuum tanker 5000 l)	100	126	1.4	1.58
Tractor (self-loading-trailer)	100	13.5	0.3	0.75

*The functional unit (FU) selected is 1 ha of alfalfa/cycle. On average, one cycle equals 4.5 years. Diesel and oil are given as litres per functional unit (L/FU).

Energy data for the cultivation subsystem are given Table 2.9. The data were adopted from a life cycle study by Adler et al. (2007) in Pennsylvania, USA; their research concerned five bioenergy cropping systems, ie. corn, soybeans, alfalfa, hybrid poplar, reed canarygrass, and switchgrass.

Table 2.9: Fossil-fuel energy requirements from agricultural machinery, reported by (Adler et al. 2007).

Farm operation	Conventional tillage		No-till	
	Fuel usage (l/ha)	Energy (GJ/ha)	Fuel usage (l/ha)	Energy (GJ/ha)
Tillage				
Plough	20.5	0.78	-	-
Disc	5.48	0.21	-	-
Crop management				
Fertilizer application	1.58	0.06	1.58	0.06
Pesticide application	263	0.1	2.63	0.1
Seeding				
Seeding year	59.89	2.32	31.33	1.21
Established stand	28	1.08	28	1.08
Final year	30.63	1.18	30.63	1.18
Harvesting				
Alfalfa mowing				
First harvest	5.09	0.2	5.09	0.2
Second harvest	4.73	0.18	4.73	0.18

The transport of biomass from field to the conversion plant is a very important step in life cycle analysis, and various logistics systems have been studied and made available for such biomass research. Logistics for alfalfa are adopted from Ecoinvent database and related literature for life cycle analysis. Several studies are found on transportation of baled or chopped biomass (Sokhansanj et al. 2006a, 2006b; Wright et al. 2006; Brechbill and Tyner 2008; Cundiff and Grisso 2008; Petrolia 2008; Morey et al. 2010). Most of the studies deal corn stover; because of its low bulk density, the transportation and handling of the biomass is very costly. Therefore, densification technologies (pellets, cubes, or briquettes) have become an important factor in biomass logistics and economics. Mowing, sun drying, baling, and transporting are the main steps in hay collection (Streeton 2005). Adapa et al. (2007) reported two different forms of obtaining dried alfalfa for further processing (Figure 2.1).

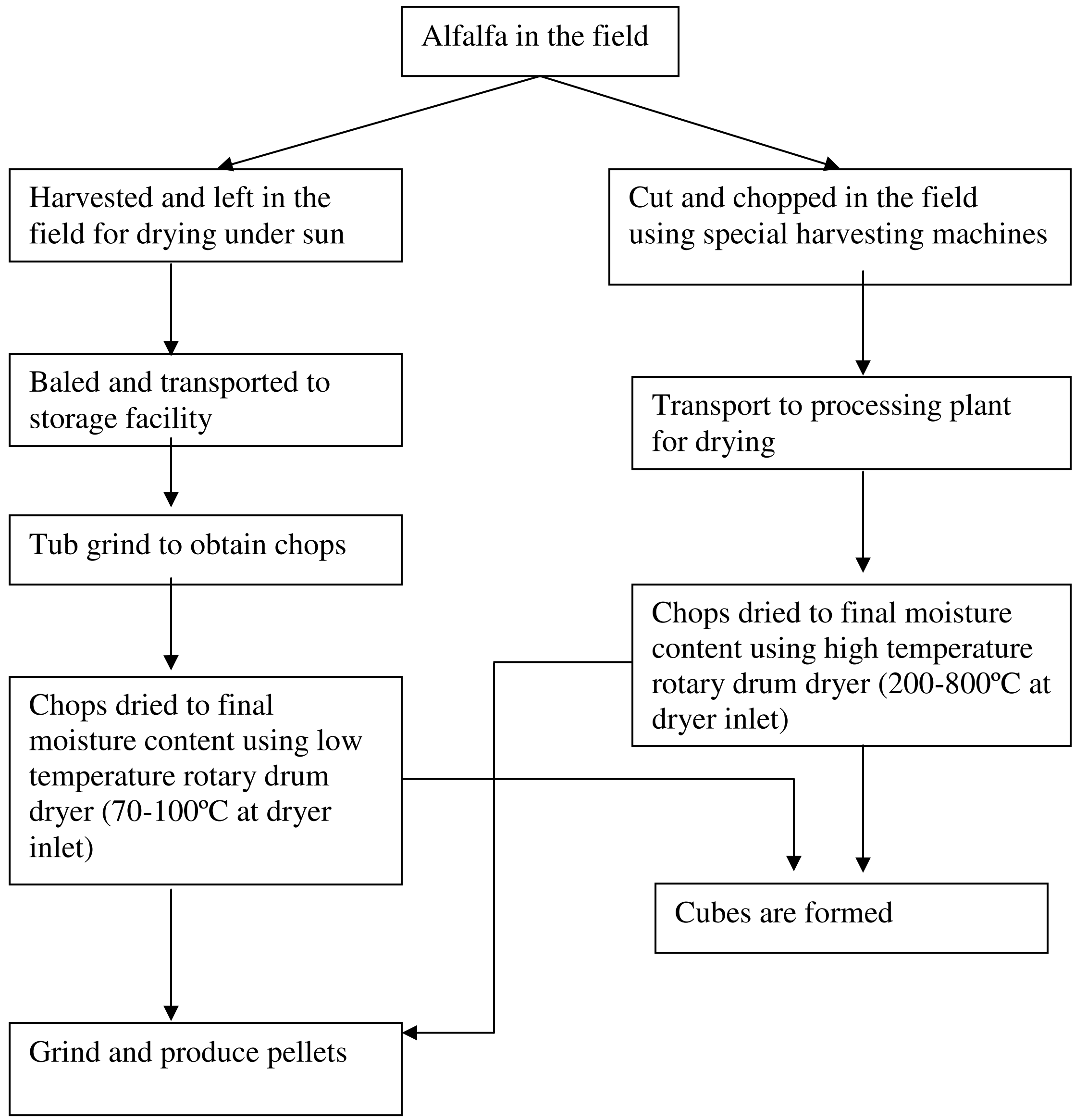


Figure 2.1: Process diagram of alfalfa drying and processing, reported by Adapa et al. (2007).

The specific input quantities required can vary with the process. Ethanol that is produced from the cellulosic feedstocks is a function of cellulose and hemicellulose content and the fermentability of the sugars. Sreenath et al. (2001) found that dejuiced alfalfa fibre consisted of 33% cellulose, 18% hemicellulose, 8% lignin, 11% protein, 9% ash, and 22% solubles. The composition of alfalfa as per literature is given in Table 2.10.

Table 2.10: Composition of alfalfa, adapted from [a] Dale (1983); [b] Sreenath et al. (2001); [c] experimental data.

Component	[a]Leaves (%)	[a]Stem/stalk (%)	[b]Alfalfa fibre (%)	[c]Alfalfa stem (%)
Cellulose	22.2	48.5	33	32.09
Hemicelluloses	11.0	6.5	18	8.09
Lignin	5.2	16.6	8	7.21
Protein	28.5	10.5	11	17.54

2.2 Lignocellulosic bioethanol processing technology

The lignocellulosic ethanol conversion system consists of four major interconnected process units: pretreatment, hydrolysis and fermentation, and distillation. There are several technologies available for each step but selection of the appropriate technique is dependent on factors such as availability, type of feedstock to be used, cost, and many others.

2.2.1 Basis of pretreatment

The first step in the production of ethanol from lignocellulosic biomass is the pretreatment of the raw biomass, to decrease the crystallinity and to increase the available surface area of the cellulose for subsequent enzymatic hydrolysis (Liu et al. 2008). This step is achieved by breaking down lignin and hemicellulose fibres which form the protective and binding matrix of plant cell walls (Hahn-Hagerdal et al. 2006). Without pretreatment, cellulase enzyme requirements for biomass ethanol production would be very high because the enzymatic hydrolysis of cellulose is an extremely slow and inefficient process as the enzymes cannot easily reach the cellulose fibres (Tolan 2006). Currently, there is no single accepted universal pretreatment method for lignocellulosic biomass because the term "biomass" includes such a diverse range of materials:

agricultural residues (straw and perennial grasses), forestry residues (softwood and hardwood), and byproducts from agricultural value-added processing such as the sugarcane or grain ethanol industry. Each of these materials requires a slightly different pretreatment process in order to obtain the highest possible sugar yield while minimizing the production of inhibitors and the degradation of lignin or hemicellulose. Koegel et al. (1999) reported liquid hot water pre-treatment (LHW or "Aquasolv") method of alfalfa fibre for ethanol production. The described conditions required pre-heated flowing water at 220^{o}C to be passed through 30 g of alfalfa fibre sample for 2 minutes at an approximate rate of 370 ml/min.

2.2.1.1 Necessity of performing pretreatment

Although pretreatment has been found to account for approximately 33% of the total production cost of converting lignocellulosic biomass to ethanol, it is a necessary step in order to achieve a commercially viable process. According to Knauf and Moniruzzaman (2004), "the criteria for successful pretreatment can be narrowed to high cellulose digestibility, high hemicellulose sugar recovery, low capital and energy cost, low lignin degradation, and recoverable process chemicals". Based on these criteria, researchers have determined that chemical pretreatment methods are more viable options than either physical or biological methods. Physical methods focus on size reduction and physical decrystallization, while biological methods use natural organisms to cause physical degradation of cellulose and lignin. Both of these methods are often self-limiting, expensive, and time consuming (Knauf and Moniruzzaman 2004).

Chemical pretreatment methods currently range from the use of hot water and steam explosion to alkaline and solvents, to acids, and to a combination of the aforementioned (Mielenz 2001). Alkaline methods are most effective at solubilizing a very high fraction of the lignin while leaving behind nearly all of the hemicellulose in an insoluble polymeric form, which can be hydrolyzed by hemicellulases (Knauf and Moniruzzaman 2004). Acid and steam or hot water methods solubilize the lignin and hydrolyze the hemicellulose fraction into a liquid phase (Liu et al. 2008). Steam and hot water pretreatment methods are often found to achieve higher sugar yields and improved enzymatic hydrolysis when an acid or alkali catalyst is added (Hahn-Hagerdal et al. 2006).

2.2.1.2 Steam explosion

Steam explosion, also known as autohydrolysis, uses pressurized steam to separate the fibres of lignocellulosic materials. During steam explosion, the lignocellulosic biomass is placed in a pressurized chamber and steam is used to saturate the pores of the material; once the pores are completely saturated, the chamber is quickly depressurized. The rapid depressurization causes the steam to instantly expand within the pores of the material, forcing the lignin matrix of the cell walls to explode, separating the fibre components; this causes the cellulose fibres to be more readily available to cellulase enzymes during subsequent enzymatic hydrolysis (Brown 2003).

Immediately before depressurization, the lignocellulosic biomass experiences hydrolysis of the hemicellulose fibres and condensation of the lignin matrix. In recent years, it has been determined that these chemical changes are in fact more significant than the mechanical deformation caused by the expanding steam. The chemical changes cause the formation of large pores in the cell walls, allowing cellulase enzymes to rapidly reach the cellulose fibres (Brown 2003). Hydrolysis of hemicellulose by steam explosion can be achieved with a high temperature and short residence time (270°C for 1 min) or with a low temperature and a longer residence time (190°C for 10 min) (Liu et al. 2008).

The main drawback of steam explosion pretreatment is that it does not result in a complete hydrolysis of hemicellulose and therefore produces a yield of only about 50% of the available hemicellulose sugars (Brown 2003). By adding an acid-catalyst, typically sulfuric or hydrochloric acid, to the steam before depressurization, it is possible to increase the hydrolysis of hemicellulose, thus increasing the hemicellulose sugar recovery during pretreatment (Hahn-Hagerdal et al. 2006). The addition of this acid-catalyst is known as dilute acid pretreatment. Another method of increasing hemicellulose hydrolysis and sugar recovery is the addition of sulfur dioxide (SO_2) gas to the biomass before steam explosion. Acid catalyzed steam pretreatment is one of the most intensively studied methods of pre-treatment, probably because of its effectiveness and inexpensive nature (Olofsson et al. 2008).

2.2.2 Saccharification and fermentation

Separate hydrolysis and fermentation (SHF) and simultaneous saccharification and fermentation (SSF) are two different techniques used for producing cellulose-based ethanol. In both of these techniques, the polymers (cellulose or hemicellulose) are broken down into simple sugars, namely hexose (six-carbon [C6] sugars mainly glucose and mannose) and pentose (five-carbon [C5] sugars, mainly D-xylose and L-arabinose) which are fermented into ethanol. Fermentation of most available C6 and C5 sugars to ethanol is crucial to the economics of these processes because it maximizes the ethanol and co-product yield while minimizing the cost of waste by-product disposal. Cellulase production, over the last decade has greatly increased through the application of several biotechnological advances. Cellulase enzyme breaks down the complex cellulose structure into fermentable sugars; the latter are used by yeast to produce ethanol.

Most yeast strains, such as *Saccharomyces cereviceae,* are capable of converting six-carbon sugars (glucose, etc.). In fact, *S. cereviceae* is considered the pre-eminent microorganism for industrial production of ethanol, with research efforts aimed at engineering recombinant *S. cereviceae* yeast strains for increasing the ethanol yield. Choosing an appropriate mechanism to ferment the C5 sugars of the hemicellulose fraction is also important. In the study by Koegel et al. (1999), both five- carbon and six-carbon sugars were fermented by genetically modified yeast, *Candida shehatae* FPL-702 and FPL-049. The experiment was carried out for both treated and untreated alfalfa fibre using the simultaneous saccharification and fermentation (SSF) technique.

The use of SSF reduces the number of fermentation/hydrolysis vessels required and reduces the chance of contamination (Aden and Foust 2009). It has been estimated that this technology reduces capital costs by more than 20% (Olofsson et al. 2008; Wingren et al. 2003). In addition, SSF may help to improve fermentation by the fermentative organisms converting compounds that would otherwise inhibit enzymatic hydrolysis (Tengborg et al. 2001; Aden and Foust 2009). Production costs were cut by 22% for corn-stover feedstock in an SSF facility, as well as ethanol production being increased by 42% (Sassner et al. 2008). There is substantial research in the areas of SSF (Krishna et al. 2000).

2.3 Life cycle analysis

Life cycle assessment (LCA) has been used over the past four decades, starting from late sixties and early seventies (Jensen et al. 1997). In LCA, environmental aspects of all stages of a product's life are analyzed from the extraction of raw materials needed to make the product to its final distribution. For instance, resource utilization and environmental impacts associated with beverage containers were studied in 1969 with research funded by the Coca Cola Company. In the early years of life cycle assessment studies, the focus was mainly on energy use. However, by the mid eighties and early nineties, the scope was broadened to include other areas (Jensen et al. 1997).

Ometto and Roma (2010) defined LCA as "an objective process to evaluate environmental loads or impacts associated with products, processes or activities, based on the identification and quantification of the energy and materials used, as well as of the wastes emitted into the environment". Garcia et al. (2010b) and International Organization for Standardization 14044 (1996) defined LCA as a methodology for assessing environmental impacts of a product throughout its life cycle by evaluating resource consumption and emissions. The generic process flow of lignocellulosic ethanol is given in Figure 2.2.

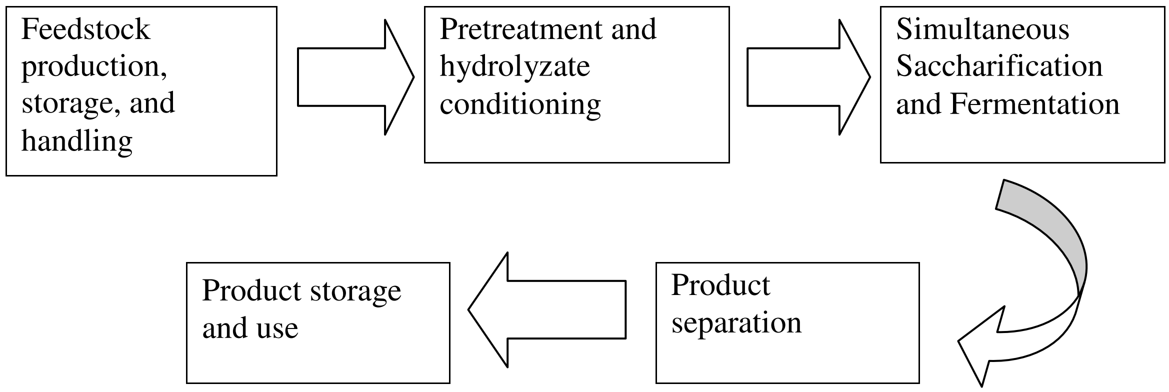


Figure 2.2: The overall process diagram of converting cellulosic biomass into ethanol.

For ease in handling and utilization of data, the whole life cycle of the product or process can be divided into subsystems, namely feedstock production subsystem (agricultural subsystem), ethanol conversion subsystem, and blending and vehicle operation subsystem. As Garcia et al. (2010a, 2009a, 2009b) and Yu and Tao (2009) described the methodology of LCA, the system boundaries for a biomass-based ethanol life cycle includes cultivation, extraction, final processing, and end use. Based on the ISO standard [International Organization for Standardization (ISO), 14040 (1996)] and Kluppel (1997), each LCA study consists of four interrelated steps: a) goal and scope definition; b) life cycle inventory (LCI) during which input and output data are collected and analyzed; c) Life cycle impact assessment (LCIA); and d) interpretation of results.

2.3.1 Goal and scope definition

Goal and scope definition is the first phase of LCA which contains goal, scope, functional unit, system boundaries, and data quality (Jensen et al. 1997). The goal defines the purpose of the study, intended use of the results, and users of the results. The scope provides the border of the assessment, providing the breadth, depth and the detail of the study. The functions of the system, functional unit, system boundary, allocation procedures, data requirement, assumptions, and limitations are included in this section (Jensen et al. 1997). Research gaps exist with regard to the allocation method and scope definition (Luo et al. 2009a). For the LCA of lignocellulosic bioethanol, system boundaries include inputs (fertilizer, energy, and agrochemicals required for the production of the feedstock), mechanisms (such as harvesting and transportation of the feedstock to the ethanol plant), and emissions associated with ethanol production. It is quite debatable which assumptions are to be incorporated in the LCA analyses. Most of these assumptions are based on the availability of data specific to the site or process.

Garcia et al. (2009a) carried out research on flax shive-based fuel ethanol in flexi- fuel vehicles and they divided the system into five subsystems:

Subsystem 1 – Agricultural: This subsystem relates to agricultural field operations including field preparation, ploughing, harrowing, sowing, fertilizing, pesticide application, harvesting, and the post-preparation steps.

Subsystem 2 – Bales formation: This subsystem included scutching, baling, and storing of flax shives until transportation to the refinery for processing.

Subsystem 3 – Material processing: This relates to processing of biomass into ethanol. The steps involved are feedstock storage and handling, pretreatment and hydrolyzate conditioning, simultaneous saccharification and fermentation, product separation and purification, waste water treatment, product storage, lignin combustion, and energy and enzyme production. This processing is considered as the most important subsystem and is called the ethanol refinery subsystem. Airborne emissions and ethanol from the feedstock production are considered as major outputs of this subsystem.

Subsystem 4 – Blending: Preparation of ethanol blends (E_{10} and E_{85}) and their storage before use in a vehicle is considered in this subsystem. It also included gasoline production, transportation of ethanol blends to the regional storages, and pure ethanol and gasoline transportation to the regional stations.

Subsystem 5 – Combustion: Utilization of the fuel in the flexi fuel vehicles is part of this subsystem. The emissions are quantified according to the amount of gasoline and ethanol needed to drive 1 km of distance.

Functional unit is the foundation of an LCA which sets the scale for comparison. The functional unit is defined to compare the systems on the same quantitative basis. Therefore, all the energy and mass flows in the inventory are normalized to this functional unit (Kadam 2002). The efficiency, durability, and performance quality of a product have to be taken into account when defining its functional unit. All data collected in the inventory phase are related to a functional unit (Table 2.11), providing a reference to which the input and output data are normalised.

Table 2.11: Functional unit referring to different studies.

Index	Functional unit	Reference
1	1 km driven by passenger car	Fu et al. 2003
2	1 dry ton of bagasse	Kadam 2002
3	1 ha of arable land producing biomass for biofuels for a 40 year period	Kim and Dale 2005
4	1 km driven by a middle size flexi fuel vehicle (FFV)	Garcia et al. 2009a
5	1 kg of pure ethanol and 1 km distance covered by an ethanol fuelled vehicle	Garcia et al. 2009b
6	1 ha of land and 1 km travelled using 85% ethanol in gasoline (E85) versus gasoline	Sheehan et al. 2008

2.3.2 Life cycle inventory (LCI)

This is the most time consuming step. It entails identifying and quantifying resources used (including energy, raw materials, and capital), as well as waste and emissions generated at each phase of production in the entire life cycle of a product or process. A major part of any life cycle analysis is data collection of such inputs and outputs of the production cycle (Garcia et al. 2009b). The quality of the data has a large impact on the quality of LCA results. Table 2.12 shows some of the important data needed for the analysis as listed by Garcia et al. (2009a) for flax shive-based fuel ethanol production.

Table 2.12: Required data for the life cycle inventory of lignocellulosic ethanol, reported by Garcia et al. (2009a).

Sub system	Data required
Agriculture sub system	Fuel use Fertilizer use Pesticide use Labour use Consumable material transport (mode, capacity and distance) Nutrient related emissions
Bales formation sub system	Fuel use Weight of bales Bales transport (mode, capacity and distance)
Ethanol refinery sub system	Production capacity Chemical use Nutrient use Enzyme production Landfill operation Consumable material transport (mode, capacity and distance) Energy requirements Industrial equipment use

The data required in Table 2.12 builds up the life cycle inventory (LCI). There are a number of publications that provide the basics for LCA and input data relevant to the production process. Kadam (2002) has listed some of the sources for basic aspects of life cycle inventory (LCI) and life cycle impact assessment (LCIA), such as publications from the Society of Environmental Toxicology and Chemistry (SETAC 1993), the US Environmental Protection Agency (Bakst et al. 1995; Keolelan and Menerey 1993; Vigon et al. 1993), and the International Organization for Standardization (1996). The data for alfalfa LCA are acquired from different sources and methods including field data, research reports, farmers and resource personnel interviews, and literature review.

Life cycle models are obtained from various types of LCA software such as SimaPro and Umberto (Uihlein et al. 2008). The Boustead Model, version 5.0, is an LCI database which provides information on fuel and energy use, raw material requirements, solid, liquid, and emissions related to transportation or diesel and electricity production (Kemppainen and Shonnard 2005). Environmental Fate and Risk Assessment Tool (EFRAT) [Version 1.0.44.] along with information from Aspen Plus simulation was used for quantifying emissions in Kemppainen and Shonnard's (2005) study. Table 2.13 summarizes some of the models and software used for LCA analyses.

Table 2.13: Models and software used in life cycle analysis.

Index	Model/ Software	Reference
1	SimaPro 4.0	Fu et al. 2003 Gasol et al. 2007
2	DAYCENT model	Kim and Dale 2005
3	GHGenius	Spatari et al. 2005 Wisemer et al. 2006
4	GREET model	Shapouri et al. 2004 Wang et al. 2007
5	Aspen Plus	Carpentieri et al. 2005 Cherubini et al. 2009 Gnansounou et al. 2009 Kemppainen and Shonnard 2005
6	Tools for Environmental Analysis and Management (TEAM) by Ecobalance, Inc.	Mann and Spath 2001
7	The software package Chain Management by Life Cycle Assessment	Luo et al. 2009a
8	Energy and Resources Group Biofuel Analysis Meta-Model (EBAMM)	Schmer et al. 2008
9	TEAM (Tools for Environmental Analysis and Management)	Heller et al. 2003

2.3.3 Life cycle impact assessment (LCIA)

The third phase of life cycle study is impact assessment, which evaluates the results of the LCI to understand their significance. It translates or converts inventory results obtained from the LCI into consequences in what could also be a qualitative or quantitative process (Consoli et al. 1993; Burgess and Brennan 2001). According to the definition, impact assessment has to be transparent and effective in terms of cost and resource use. LCIA contains four main elements: category definition, classification, characterization, and valuation (Jensen et al. 1997). Each of these elements represents a specific procedure, but all elements are not required for all applications. Impact categories describe impacts associated with a product system being considered. For instance, abiotic resources, biotic resources, land use, global warming, stratospheric ozone depletion, ecotoxicological impacts, human toxicological impacts, photochemical oxidant formation, acidification, eutrophication, and work environment are considered as impact categories (Jensen et al 1997). The second element of LCIA is classification, which assigns the inventory input and output data to potential environmental impacts listed above. Global impacts, regional impacts, and local impacts are three different divisions into which the impact categories are grouped. Quantification of environmental processes by scientific analysis is called characterization; it assigns the relative contribution of each input and output to the selected impact categories. As different impact categories have different units, they are plotted on a percentage scale. These quantified impact categories are weighted during valuation. There are different weighting methods available, such as proxy approach, technology abatement approach, monetarization, distance to target, and authoritative panels. Each method focuses on different impacts (Jensen et al. 1997).

2.3.4 Interpretation of results

According to International Organization for Standardization (1997), interpretation is composed of specific steps: i) identification of significant environmental issues; ii) evaluation; and iii) conclusions and recommendations (Jensen et al. 1997). These steps involve an interpretation of LCA results for communication; for process, product, or design changes, or for further purposes. Sensitivity analyses identify and check the effects of critical data on the results. They can be conducted by systematically changing input parameters. Uncertainty analyses check the effect of uncertain data (e.g. estimated or approximated data). Variation analyses assess the effect of alternative scenarios and life cycle models.

2.4 Life cycle based energy and environmental impact studies

The studies on biofuels can be categorized according to their feedstock and major findings. Most of the research is based on analyzing environmental impacts (for example, greenhouse gas emission) and net energy balance. There are numerous studies on starch (grain) or sugar-based ethanol (Nguyen and Gheewala 2008; Huang et al. 2008; Kwiatkowski et al. 2006). However, research on the lignocellulosic ethanol pathway is still emerging and is given more attention in countries such as Canada. Sugarcane bagasse (Kadam 2002), corn stover (Sassner et al. 2008; Aden and Foust 2009; Sokhansanj et al. 2010), grain straw (Kerstetter and Lyons 2001; Pahkala et al.2007) wood residue (Kemppainen and Shonnard 2005; Kumar et al. 2010; Zhang et al. 2009; Tu et al. 2007), and energy crops (Cherubini et al. 2009; Garcia et al. 2009b ; Schmer et al. 2008; Spatari et al. 2005; Sassner et al. 2008) are some of the lignocellulosic feedstocks of interest to researchers. Nguyen and Gheewala (2008) conducted a well-to-wheel analysis of cassava-based ethanol in Thailand. An LCA of electricity production from willow biomass was conducted in New York state (Heller et al. 2003) using TEAM (Tools for Environmental Analysis and Management) software. A comparative LCA of timber and newsprint for cellulose-based biomass-to-ethanol pathways was conducted by Kemppainen and Shonnard (2005). This section summarizes available life cycle studies on biofuels.

Studies on energy and GHG balances in biofuels are biased in their system definition and boundaries, allocation methods, functional units, types of blend, and various modelling choices. Gnansounou et al. (2009) conducted a detailed literature survey on well- to- tank (WtT), tank- to- well (TtW) and well- to- wheel (WtW) studies. Figure 2.3 shows stages covered in the GREET model for fuel cycle analysis (Wang 2001).

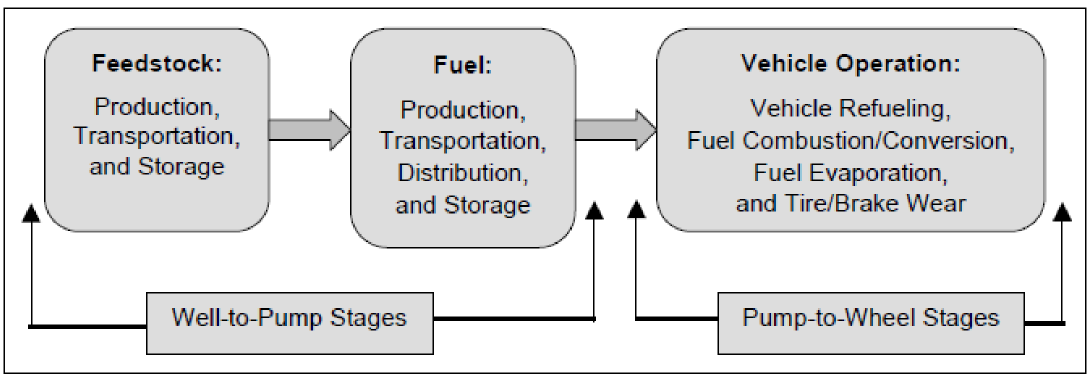


Figure 2.3: Stages covered in GREET fuel-cycle analysis, reported by Wang (2001).

Well-to-wheel (WtW) is also called fuel cycle analysis, which consists of feedstock, fuel, and vehicle operation stages. The combination of feedstock and fuel stage is called WtT. Tank-to-well (TtW) stage is also called pump-to-well (PtW), which comprises the vehicle operation stage.

The energy used at each stage of the life cycle is one mirror image of the overall environmental performance of the system. Quantification of total energy demands and the overall energy efficiencies of processes and products can be performed using life cycle inventory (Kadam 2002). Kadam (2002) reported different types of energy flows which facilitate clear understanding of the analyses. They are comprised of total primary energy, feedstock energy, process energy, fossil or non-renewable energy, and renewable energy. Total primary energy includes the cumulative energy of all resources extracted from the environment, i.e. the energy of all raw materials. Feedstock energy and process energy are subsets of primary energy, and they can be fossil or non-fossil energy. Energy contained in the biomass is termed as feedstock energy and is directly constituted in the final product. Process energy refers to the energy contained in the life cycle excluding feedstock energy (Kadam 2002). Energy expenditure within the system is to be tracked so that the net energy production can be assessed. Two types of energy accounted for are i) energy used directly in each process block; and ii) energy contained in the materials used in each process block. To determine net energy in LCA, the energy used directly in these categories is subtracted from the energy produced by ethanol combustion. A wide range of research and peer-reviewed data are incorporated into the model.

According to the comparative LCA study by Kemppainen and Shonnard (2005) on cellulosic ethanol production from two lignocellulosic feedstocks (virgin timber resources and recycled newsprint from an urban area), the timber process showed less electricity consumption and less emission while the newsprint process was considered less energy efficient. Heat integration is identified as the process improvement. The energy requirements for producing ethanol over the life cycle of both processes are 14% and 27%, respectively. The foundation for conducting LCA is obtained from Aspen Plus simulation model produced by NREL, using yellow poplar as the feedstock.

Schmer et al. (2008) studied the net energy balance and economic costs of cellulosic ethanol derived from switchgrass with known farm inputs and harvested yields. The results concluded that switchgrass produced more than 500% renewable energy than non-renewable energy consumed in its production. The GHG emission was estimated to be 93% lower than the estimated GHG from gasoline. For these conclusions, LCA was conducted using Energy and Resources Group Biofuel Analysis Meta-Model (EBAMM) which calculated agricultural inputs and yields of switchgrass, transportation costs, energy of ethanol, plant materials, and related factors.

According to Nguyen and Gheewala (2008), their cassava-based ethanol production revealed that process energy was three fold: fuel oil, biogas and fuel oil, and biogas and rice husk. The result showed that the incorporation of biomass to obtain process energy significantly affected the performance of E85 blend. Overall, ethanol blended gasoline showed lower levels of GHG emission.

Lignocellulosic ethanol pathway and GHG emission associated studies are of continuing interest to researchers. Cellulose ethanol derived from switchgrass, blended with vehicle performance, was studied by Spatari et al. (2005) in order to evaluate environmental benefits in the near and midterm timeframes. The comparison has been made with low sulphur reformulated gasoline (RFG) and E85 fuelled automobiles. Near-term LCA results showed GHG emission was 57% lower from switchgrass derived E85 cellulosic ethanol in a blended-fueled vehicle and 65% lower for corn stover ethanol than RFG. The life cycle model incorporates process inputs and outputs such as energy (total and renewable), GHG (CO_2, CH_4, and N_2O) and other pollutants, cultivation and transportation data of feedstocks, data on the conversion process, and distribution from scientific literature and models (GHGenius and GREET).

Emissions from direct and indirect fuel use, N_2O emissions from fertilizer and leaf litter, carbon sequestration in below ground biomass, and soil carbon were estimated by Heller et al. (2003). It was concluded that willow biomass is an efficient bioenergy feedstock.

Ethanol from *Brassica carinata* was studied by Garcia et al. (2009b), using enzymatic hydrolysis process. Two ethanol blends (E10 and E85 in passenger cars) were evaluated for environmental performance. Two functional units were defined: 1kg of pure ethanol and 1 km distance covered by an ethanol fuelled vehicle. In this study, the ethanol conversion process was divided into nine steps, namely:

(i) feedstock handling and storage;

(ii) pre-treatment and conditioning;

(iii) saccharification (or enzymatic hydrolysis) and co-fermentation;

(iv) distillation and dehydration to purify and concentrate the ethanol up to 99.5%;

(v) storage of ethanol;

(vi) wastewater treatment;

(vii) energy production (electricity and heat process) from solids from distillation, syrup, and biogas;

(viii) enzyme production (all enzymes needed in the process are produced in their own plant); and

(ix) ancillary utilities, which include the production of cooling, sterilizing, and processing water as well as compressed air.

From the study, E85 ethanol blend was identified as the best option for reducing GHG emissions in terms of a travel distance functional unit. Overall, ethanol-based fuel was reported to reduce global warming and fossil fuel consumption.

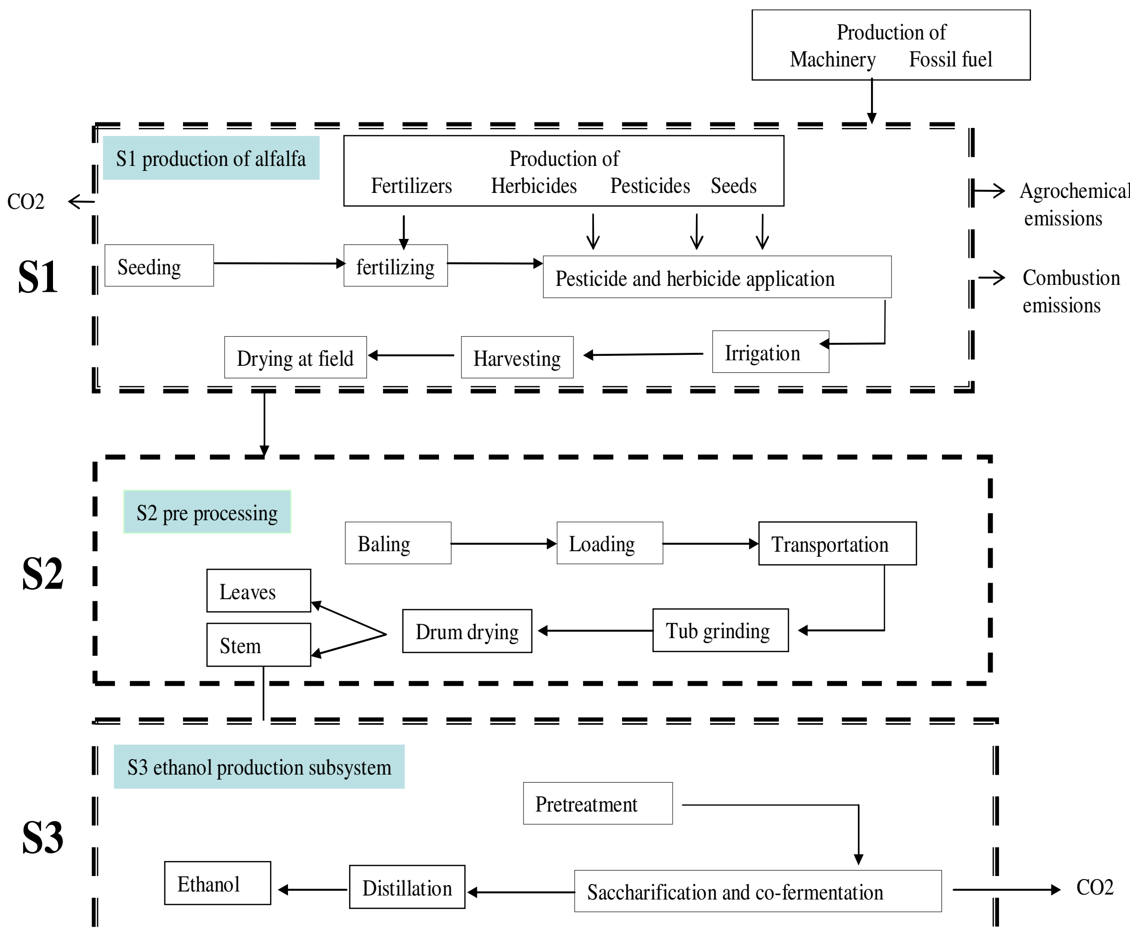
The complication of determining energy balance and GHG emission was explained by Cherubini et al. (2009). The study included different combination of feedstocks, conversion routes, fuels, end-use applications, and methodological assumptions. The study concluded with contradictory results relevant to liquid biofuel systems for lignocellulosic ethanol. They are: i) biomass to liquid fuel pathway consumes more fossil fuel compared to biomass to electricity and heat processes; ii) GHG emissions by perennial grasses (eg: switchgrass and *Miscanthus*) is low as they enhance carbon sequestration in soil; iii) use of waste products and residues in bioenergy systems provide best LCA outcomes; and iv) co-product and process residues as raw materials in conversion plants result in fossil energy saving and GHG mitigation.

2.5 Summary

The literature related to this research is reviewed in this section. It is based on literature covering alfalfa production, processing, and life cycle analysis of different lignocellulosic feedstocks. It provided information on the current status of alfalfa cultivation in Canada and the biological, physiological, and agronomic aspects of the crop. Literature values of yield, inputs in production and supporting information in deriving necessary assumptions are described in detail. This chapter also included the ethanol conversion technology adopted in this study. The main process steps are pretreatment, enzymatic hydrolysis, fermentation, and distillation. Different technologies associated with each process steps are described in subsection two. Since there was a general lack of literature data relevant to ethanol plant energy for each process, cumulative energy values for corn stover in 10 different studies were considered for the analysis as given in chapter 3. As well, the final subsection provides a thorough literature survey of life cycle analysis on lignocellulose-based ethanol made from different feedstocks for use as transportation fuel. The review in this section focused on mechanisms and methods of LCA, LCA of bioethanol productions, assumptions used, and findings obtained. Most of the LCA studies, though, were conducted in Europe. Therefore, there is a need to conduct LCA on alfalfa stem-based bioethanol production within a Canadian context in order to make reliable decisions.

3. Methodology

This study consists of cradle- to-gate life cycle analysis of lignocellulosic biomass to ethanol derived from alfalfa stems. Figure 3.1 presents a simplified version of the system boundaries, starting from the alfalfa cultivation. All input and output flow along the full chain for producing, collecting, and processing the feedstock into biofuel.



----- Subsystem boundaries

Figure 3.1: System boundaries of alfalfa stem based bioethanol.

3.1 Goal and scope definition

The objective of this study is to identify environmental impacts of ethanol production using alfalfa stem biomass. The life cycle of bioethanol derived from alfalfa stem is assessed in terms of five impact categories: i) abiotic resource depletion (AD); ii) acidification (A); iii) eutrophication (E); iv) global warming (GW); and v) human toxicity (HT).

3.2 Functional unit

All inputs and outputs of the product system are related to the functional unit, which is 1 kg of dry alfalfa input and 1 L of ethanol output. This unit provides a reference for the detailed analysis of the process presented in this research.

3.3 System description and data input

This study is divided into three subsystems: alfalfa cultivation subsystem (S1), baling and pre-processing subsystem (S2), and ethanol conversion subsystem (S3). Figure 3.1 depicts a detailed description of the unit processes and subsystems considered within the system boundaries. There are two different types of data involved: primary and secondary data (SETAC 1993). Primary data here refers to data obtained from individual production plants and companies. Secondary data includes data from published sources such as databases, industry or government publications, journals, or books; the term also includes unpublished data (and educated guesses) from experts based on their knowledge of the field. This study significantly utilized the latter data type, mainly obtained from peer reviewed literature, government reports, books, and personal communications.

3.3.1 Cultivation subsystem (S1)

The cultivation subsystem consists of all agricultural field operations including field preparation, seeding, fertilizer application, pesticide and herbicide application, irrigation, and harvesting. There are two products in alfalfa cultivation: i) protein-rich leaves which can be used as livestock feed (animal fodder); ii) alfalfa stems as agricultural residue which can be used for ethanol production. The inputs include seed, fertilizer, pesticides, herbicides, agricultural machinery (for field preparation, irrigation, agrochemical application, sowing, harvesting, and drying), and labour (farmers' transport to cultivate and manage the crop). In this subsystem, transportation of all the materials is taken into account. The following activities in this subsystem are excluded from the LCA analysis:

i) Emission from agrochemical application;

ii) Emission associated with machinery use for field preparation, irrigation, agrochemical application, seeding, harvesting, haying, and drying; and

iii) Labour use.

3.3.1.1 Site selection

As reported by other studies, western Canadian alfalfa has been grown under irrigation in Saskatoon and Outlook, Saskatchewan (Gossen et al. 2004), southern Alberta (Government of Alberta 2010; Moyer et al. 1991), and southwestern Saskatchewan (Swift Current, SK) (Jefferson and Gossen 2002). For this study, the selected alfalfa cultivation area is located in Saskatoon, and the feedstock is collected from a 100 km radius. This selection was based on Census of Agriculture data for 2001 and 2006 for alfalfa cultivation (Statistics Canada 2006). Table 3.1 depicts seeded hectares of alfalfa mixtures in Saskatchewan, classified by Census Agricultural Region (CAR) and Census Division (CD). Approximately 80% of this cultivation consists of a mixture with other crops. However, it is assumed that the 100 km radius provides a sufficient amount of raw material for a 25 million litre capacity ethanol plant. According to theoretical calculations of raw material supply, the operation of an ethanol plant with a capacity of 25 million litres per year requires approximately 12 x 10^3 ha and 19 x 10^3 ha of irrigated and non-irrigated alfalfa, respectively. There are more than 80 x 10^3 ha of alfalfa reported in the Saskatoon region, as shown in Table 3.1. The selected Saskatoon region is located in the dark brown soil zone of Census Agricultural Region 6B (Figure 3.2 and Figure 3.3).

Table 3.1: Seeded hectares of alfalfa mixtures in Saskatchewan under Census Agricultural Region (CAR), classified by Statistics Canada (2006).

Geography	2006		2001	
	Farms reporting	Hectares	Farms reporting	Hectares
Saskatchewan - PR (470000000)	18,417	1,592,206	17,297	1,142,343
Agricultural Region 1A - CAR (471000000)	849	79,995	799	53,796
Agricultural Region 1B - CAR (471100000)	881	74,597	828	47,392
Agricultural Region 2A - CAR (472000000)	519	51,478	391	24,210
Agricultural Region 2B - CAR (472100000)	923	64,520	800	42,746
Agricultural Region 3AN - CAR (473000000)	548	64,237	473	38,898
Agricultural Region 3AS - CAR (473100000)	930	110,448	754	69,283
Agricultural Region 3BN - CAR (473200000)	912	69,805	802	44,872
Agricultural Region 3BS - CAR (473300000)	586	69,134	518	38,740
Agricultural Region 4A - CAR (474000000)	530	60,797	447	37,284
Agricultural Region 4B - CAR (474100000)	289	23,253	195	14,055
Agricultural Region 5A - CAR (475000000)	1,431	104,568	1,370	70,526
Agricultural Region 5B - CAR (475100000)	1,530	119,511	1,621	101,942
Agricultural Region 6A - CAR (476000000)	1,223	108,265	1,051	65,294
Agricultural Region 6B - CAR (476100000)	1,319	103,770	1,320	80,138
Agricultural Region 7A - CAR (477000000)	359	26,443	264	16,148
Agricultural Region 7B - CAR (477100000)	536	36,076	519	27,594
Agricultural Region 8A - CAR (478000000)	997	86,133	1,143	82,245
Agricultural Region 8B - CAR (478100000)	692	41,466	602	26,241
Agricultural Region 9A - CAR (479000000)	1,952	153,272	1,992	136,837
Agricultural Region 9B - CAR (479100000)	1,411	144,440	1,408	124,103

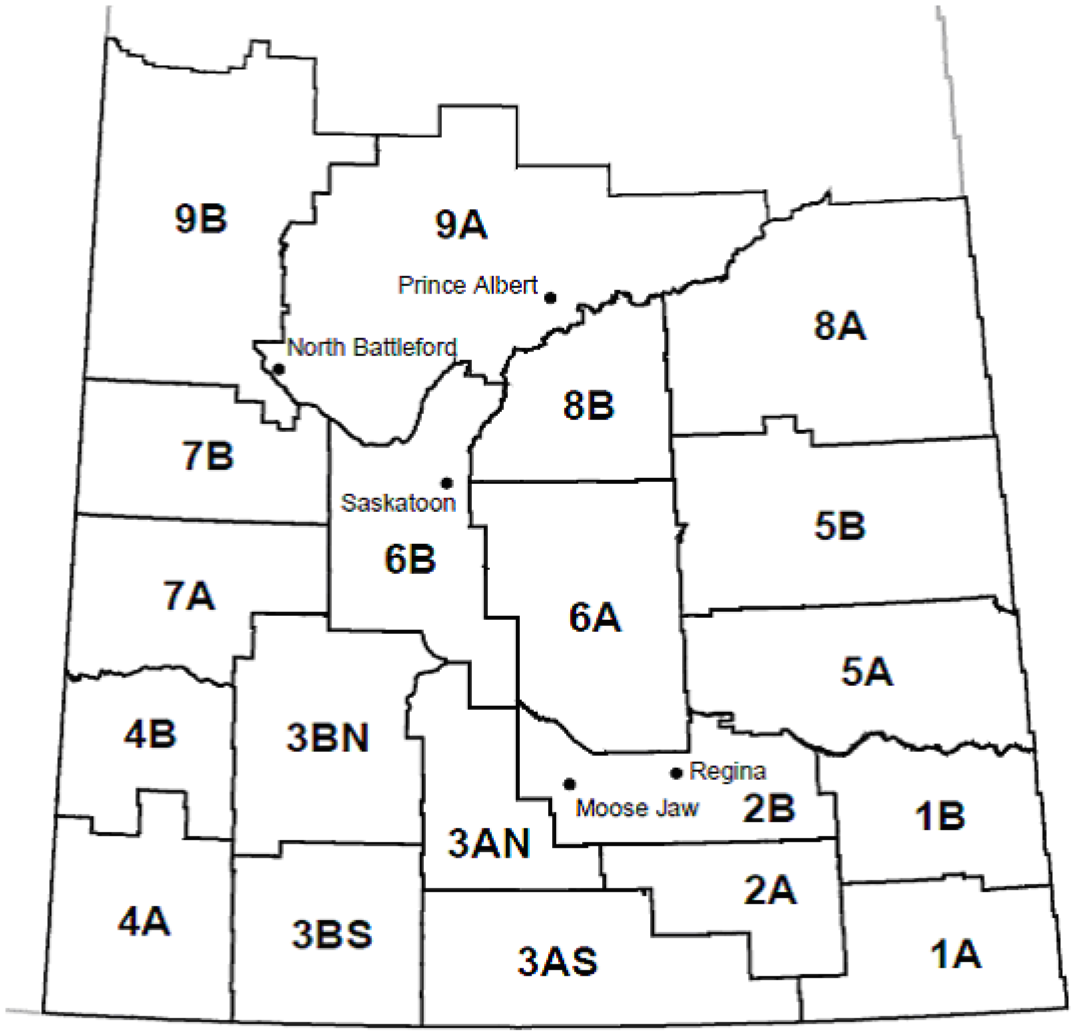


Figure 3.2: Census Agricultural Regions (CAR) of Saskatchewan, reported by Statistics Canada (2006).

Figure 3.3: Soil zones of Saskatchewan, reported by Saskatchewan Ministry of Agriculture (2010a).

3.3.1.2 Input selection

The variety "Beaver" was selected from among the various alfalfa varieties grown in this area. Yield is assumed to be 11 x 10^3 kg/ha with irrigation and 7000 kg/ha without irrigation (Table 2.6: Saskatchewan Ministry of Agriculture 2010b). These two aspects were used to conduct life cycle analysis in SimaPro (PRE Consultants, Amersfoort, Netherlands). The input data were obtained from published literature, government reports, and fact sheets. Inputs for cultivation of 1 ha of alfalfa are given in Table 3.2.

Table 3.2: Input requirements for cultivating 1 ha of alfalfa.

Input	Amount	Reference
Seed	9.00 kg	Saskatchewan Ministry of Agriculture 2010a
Fertilizer		
Nitrogen	3.67 kg	Saskatchewan Ministry of Agriculture 2010c
Phosphorous	36.71 kg	Government of Alberta 2010
Potassium	27.54 kg	Government of Alberta 2010
Sulfur	5.51 kg	Government of Alberta 2010
Manure/ compost	4046.86 kg	Government of Alberta 2010
Agrochemicals		
Herbicides (Glyphosate)	0.14 kg	0.84 kg/ha Loux et al. 2010
Pesticide (Indoxacarb)	0.63 kg	0.49-0.83 L/ha Youngman 2010
Irrigation water	444.44 m^3	Gallego et al. 2007
Electricity consumption	2437 KW/h	Gallego et al. 2007

Seeding rate is dependent on seeding date, soil type, and type of production. In this study, seeding data were gathered from Forage Crop Production Guide (Saskatchewan Ministry of Agriculture 2011). Seeding rate for both dark brown soil and irrigated soil is 9 kg/ha (Saskatchewan Ministry of Agriculture 2010a) (Table 2.3).

Fertilization of alfalfa is not very common in Saskatchewan (Welford, R., Asst. Professor, Department of Chemical and Biological Engineering, University of Saskatchewan, Personal Communication). However, in this study, a worst case scenario was considered where fertilizer application was taken into account. The fertilizer application rate is based on government fact sheets. According to the literature, most Saskatchewan soil is deficient in nitrogen and phosphorous. Alfalfa as a leguminous crop that fixes 80% of its nitrogen demand through its symbiotic relationship with Rhizobium, a soil bacterium; in fact, Rhizobia are a unique type of soil bacteria precisely because they live in symbiotic relationships with legumes. However, depending on the soil condition of a given region, a small amount of nitrogen fertilizer is assumed to be applied (Table 3.2) (Saskatchewan Ministry of Agriculture 2010c). Alfalfa is a high sulphur consuming crop; therefore, a sulphur deficit can also be observed in this crop, and it is reported that an area of 0.45 x 10^6 ha in Saskatchewan shows potassium deficiency (Saskatchewan Ministry of Agriculture 2010c). The calculation of fertilizer was based on all of the aforementioned factors.

The use of agrochemicals for alfalfa cultivation is critical. For a vigorous cultivation, herbicide application is assumed to be zero. Canada thistle and dandelion are two common weeds in alfalfa fields (Saskatchewan Ministry of Agriculture 2010c), and these two weeds belong to the broad leaf weed category. Glyphosate is assumed to be used in weed control since it is a non-selective herbicide that can be used for alfalfa; it is effective on grasses, perennials, and woody plants (Pesticide News 1996). The application rate is given in Table 3.2.

Alfalfa weevil is a chronic pest of alfalfa in southern Alberta, Saskatchewan, and Manitoba (Soroka and Georzen 2002). Therefore, it is assumed that Indoxacarb (Steward SC 1.25) is applied to control alfalfa weevil (Youngman 2010), and the application rate is given in Table 3.2.

Similar to practices employed for the majority of the crops grown in Saskatchewan, zero tillage (Welford, R., Asst. Professor, Department of Chemical and Biological Engineering, University of Saskatchewan, Personal Communication) was assumed. Therefore, a seeder was the only equipment assumed to be used during establishment. In addition, a broadcaster for fertilization of inorganic fertilizers and hydraulic loader and spreader for manure application were considered. For agrochemical application, a field sprayer was considered. It was also assumed that sun-cured alfalfa is baled and taken to the dehydration plant. Therefore, the harvesting was considered to be carried out by swathing with rotary windrower followed by haying with rotary tedder. This information was incorporated into SimaPro for the LCA. Irrigation data were adopted from Gallego et al. (2007). Two irrigation cycles (1000 m^3/ha each) are required for alfalfa cultivation, using a tractor with a 5000 L vacuum tanker, and consuming 9748 kWh/ha in electricity to pump water (Gallego et al. 2007). For SimaPro, the amount of water required for one year was averaged and incorporated.

3.3.2 Baling and pre-processing subsystem (S2)

This system consists of baling of sun-cured alfalfa and transportation to the processing plant. Transportation was assumed to be done using diesel powered trucks. At the processing plant, the harvested alfalfa biomass will undergo tub grinding (Adapa et al. 2007; Jannasch et al. 2001) which will grind the bales into 2.5-10.0 cm chops followed by drum drying which will dry the material to reduce moisture content from 40% to 12% (the sun-cured bale is usually at 16 to 20% moisture). Fractionation of ground alfalfa into leaves and stems can be done by sieving or air classification (Dale 1983). It is assumed that a modified drum dryer separates alfalfa stems from leaves during the drying process (Adapa et al. 2004). Since alfalfa yields two products, i.e., leaves and stems, allocation is needed to partition the inputs and outputs of the product. It is assumed that the crop produces leaves and stems in the same proportion; therefore, mass allocation is adopted. As such, 50% of the harvested material is considered in this subsystem for further operations, assuming that leaves were used as livestock feed. A further assumption is that the baler produces round bales (about 700 kg) (Tsatsarelis and Koundouras 1994) to be transported to the ethanol plant over a 100 km distance (which is the longest distance over which the feedstock is procured in the cultivation radius).

3.3.3 Ethanol production subsystem (S3)

In this subsystem, chopped alfalfa stems from the dehydration plant were converted to ethanol. The subsystem consists of pre-treatment, hydrolysis, saccharification, and fermentation. The conversion technology adopted here is from a study by Galbe and Zacchi (1992) on wood biomass-based ethanol production. A simplified version of the flow chart and process units are given in Figure 3.4. The mass balance of ethanol conversion is also calculated by using the data and assumptions reported above.

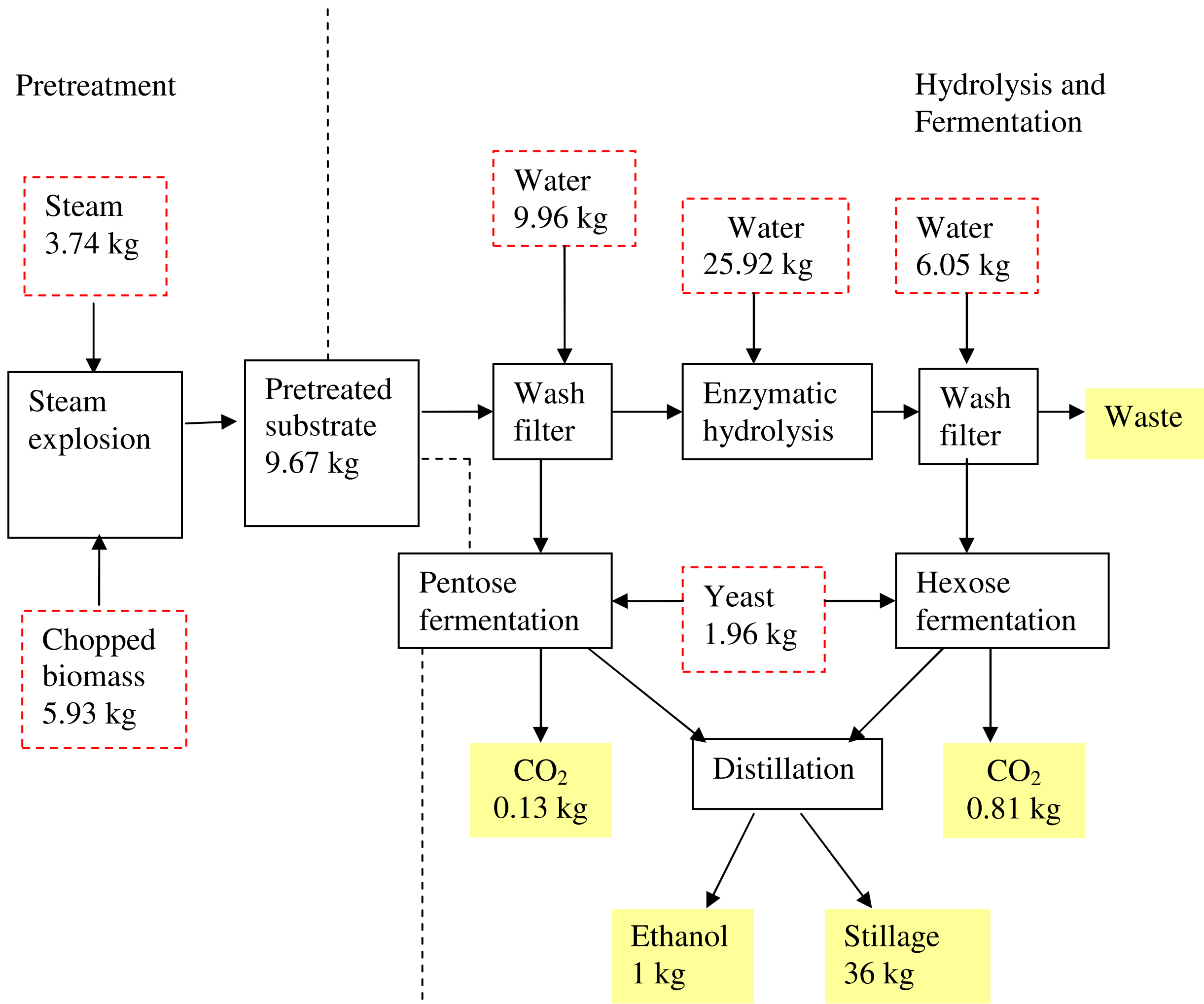


Figure 3.4: Biomass-to-ethanol process unit flow without recycling streams for 1 kg of ethanol production.

The biomass is mainly comprised of cellulose, hemicellulose, and lignin, as summarized in Table 2.10. For this study, stem composition calculated from experimental data was used for further calculations. In this work, cellulose was converted into hexose (C6) sugars, and hemicellulose was converted into pentose (C5) sugars in which both were fermented into ethanol according to the conversion technology of Galbe and Zacchi (1992).

The following assumptions were made during mass balance calculations:

i) The ethanol plant is operated for 24 hours a day and 350 days annually, and 15 days are allotted for cleaning and maintenance.

ii) Moisture content of alfalfa straw after drum drying and reception at the ethanol plant is 0%.

iii) There is no steam recycling during the process.

iv) There are no acids or gases used as catalysts during steam explosion.

3.3.3.1 Pretreatment

The biomass is pretreated by steam explosion at 220ºC during the pre-treatment step in which hemicellulose is converted into fermentable pentose. The steam requirement is given as 0.63 kg per kg of dry biomass, and the conversion efficiency of hemicellulose into pentose is 70%. The conversion step is simplified in Equation (3.1). In this step, 85% of the solubilized pentoses are recovered and directed into the fermentation (Galbe and Zacchi 1992) process. The solid material consists mainly of cellulose, un-recovered hemicelluloses, and lignin which is washed and forwarded to enzymatic hydrolysis and fermentation processes. In this step, only 59.5% hemicellulose from the substrate is available for fermentation as pentoses.

$$Hemicellulose \rightarrow Pentose + Furfural + Aceticacid \qquad (3.1)$$

3.3.3.2 Enzymatic hydrolysis and fermentation

This process unit consists of enzymatic hydrolysis and fermentation. The pretreated solid material undergoes enzymatic hydrolysis where cellulose is broken down into hexoses and non-solubilized hemicelluloses are converted to pentoses by the enzyme xylose isomerase. The enzyme loading is assumed to be 10 FPU (filter paper unit)/g or 2% (w/w), and the conversion efficiencies are 90% and 95% for cellulose and hemicellulose, respectively. It is assumed that 85% of the soluble substance is recovered from washing the material, leaving the residue with 75% moisture content (Galbe and Zacchi 1992). Enzyme production is excluded from this subsystem. During this step, fresh water is added three times: during washing of the solid material after pre-treatment, in hydrolysis, and in the adjusting of dry matter content at hydrolysis.

The sugar-rich (mostly hexoses and less pentoses) liquid is mixed with *Saccharomyces cerevisiae* (baker's yeast) to ferment into ethanol, with carbon dioxide and other compounds as byproducts. It is also reported that every 100 kg of hexoses yield 48.5 kg ethanol, 47.4 kg carbon dioxide, 1.4 kg acetic acid, and 2.7 kg glycerol (Formula 3.2) and that every 100 kg of fermentable pentoses yield 30.5 kg ethanol, 30.5 kg carbon dioxide, and 13 kg xylitol (Formula 3.3) (Galbe and Zacchi 1992).

$$Hexose \rightarrow Ethanol + CO_2 + Aceticacid + Glycerol \tag{3.2}$$

$$Pentose \rightarrow Ethanol + CO_2 + Xylitol \tag{3.3}$$

3.3.3.3 Distillation

The fermented products are sent to the distillation unit where ethanol is separated from its byproducts. During this process, 99% of ethanol is recovered and concentrated to 95% ethanol (w/w) (Galbe and Zacchi 1992). The boiling point of ethanol is 78.1^{o}C, where it is easily separated by distillation. The by-products have different relative volatilities (Table 3.3) and can be used in different industries. In this study, it was assumed that 50% and 70% recycled water was obtained from stillage and used in evaluating various LCA impact scenarios. In addition, assuming a 90% solid dry matter content for stillage and 50% protein extraction efficiency, the amount of protein residue was calculated as a byproduct. Similarly, the rest of the dry matter is calculated for fibre residue, assuming 75% solid residue moisture content. Waste water was obtained from stillage (subtracting recycled water and protein residue) and solid dry matter (75% from solid dry matter).

Table 3.3: *Relative volatilities of by-products, reported by Galbe and Zacchi (1992).

Component	Relative volatility
Ethanol	9.8
Furfural	11.2
Water	1.0
Acetic acid	0.6
Glycerol / Solubles	0.0

*Relative volatility is a measure of the differences between two components and their boiling points. It indicates how easy or difficult a particular separation will be. (http://lorien.ncl.ac.uk/ming/distil/distilpri.htm).

3.3.3.4 Energy consumption in the ethanol plant

Since incompleteness exists in available data from the literature on sub-processes involved in ethanol production, only the total energy use was applied to analyse the ethanol conversion system. Energy consumption of ethanol production from corn stover has been reported in several literature sources, and was used in this study. Table 3.4 summarizes various energy consumption values reported in previous studies with values as low as 9.5 MJ/L (Luo et al. 2009b) to as high as 21.3 MJ/L (Eggeman and Elander 2005). These values were given as input into SimaPro separately, while keeping the other parameters constant in order to evaluate the effect of changes in energy values on the final output. The results are presented in section 4.2.3.

Table 3.4: Total energy consumption of ethanol production using corn stover as feedstock from different studies.

Energy (MJ/L)	Reference
9.5	Luo et al. 2009b
12.5	Wang 2001
12.6	Sassner et al. 2008
12.9	Aden and Foust 2009
14.1	Oliveira et al. 2005
15.2	Shapouri and McAloon 2002
16.6	Graboski 2002
17.0	Patzek 2004
17.0	Pimentel and Patzek 2005
21.3	Eggeman and Elander 2005

A sensitivity analysis for LCA results was also performed in order to determine the effect of changes in energy values on the final results.

3.3.3.5 Quantification of material flow in ethanol production subsystem

The quantification model developed by Spatari et al. (2010) and conversion technology from Galbe and Zacchi (1992) were employed for constructing mass balance of S3 for different scenarios. All the metrics were relevant to the volumetric flow rate Q_E (L/h) of ethanol produced in the conversion facility. The model equation was developed by Spatari et al. (2010) and specified as follows:

$$Q_E = M_F \frac{\alpha}{\rho_{EtOH}} \times \sum_{i=1}^{n} Y_i \times Y_{i-E} \qquad (4.1)$$

where M_F is the input mass flow rate of alfalfa feedstock (kg/h); α is the ethanol recovery efficiency following distillation (which was 99%) and ρ_{EtOH} represents the density of ethanol (0.789 kg/L). The yield (by weight) of sugar i is given as Y_i, and $Y_{i\text{-}E}$ is the yield (by weight) of ethanol from sugar i, where $i = 1,2,3$ represents pentose following pretreatment of hemicellulose, hexose from hydrolysis of cellulose, and pentose from unrecovered hemicellulose fraction at the hydrolysis phase. Therefore, Y_i can be given as

$$Y_i = f_i \times c_j \times M_F \qquad (4.2)$$

The fraction of sugar polymer in the feedstock (32.09% cellulose and 8.09% hemicellulose) is represented by f_i. Conversion efficiency of converting each sugar polymer (cellulose and hemicellulose) into sugar is given by c_j. $Y_{i\text{-}E}$ can be written as;

$$Y_{i-E} = Y_i \times \beta_i \qquad (4.3)$$

where β_i is the conversion parameter for the fermentation of sugars into ethanol. Conversion parameters for hexose and pentose respectively were 48.5% and 30.5%. Equations 4.2 and 4.3 were derived based on the mass balance calculations in this study.

3.4 Software and databases

SimaPro 7.2 professional multi user version from PRE Consultants was used for life cycle analysis. SimaPro projects are made up of processes and product stages (SimaPro 7 2003). A project is an area where data are about to be collected and processed. Processes are the building blocks that contain environmental data and data on economic inputs and outputs. Processes are grouped into seven main categories, namely materials, energy, transport, processing, use, waste scenario, and waste treatment

(Figure 3.5). Each of these categories is further sub-divided into different classes and is shown in Figure 3.6.

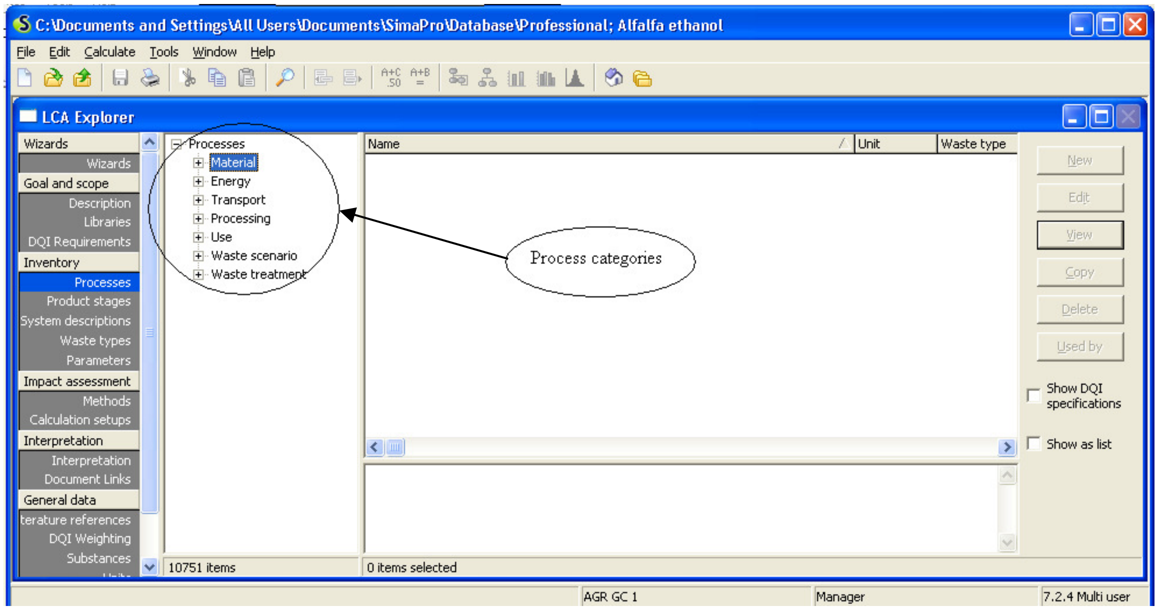


Figure 3.5: Overview of the major process categories in SimaPro.

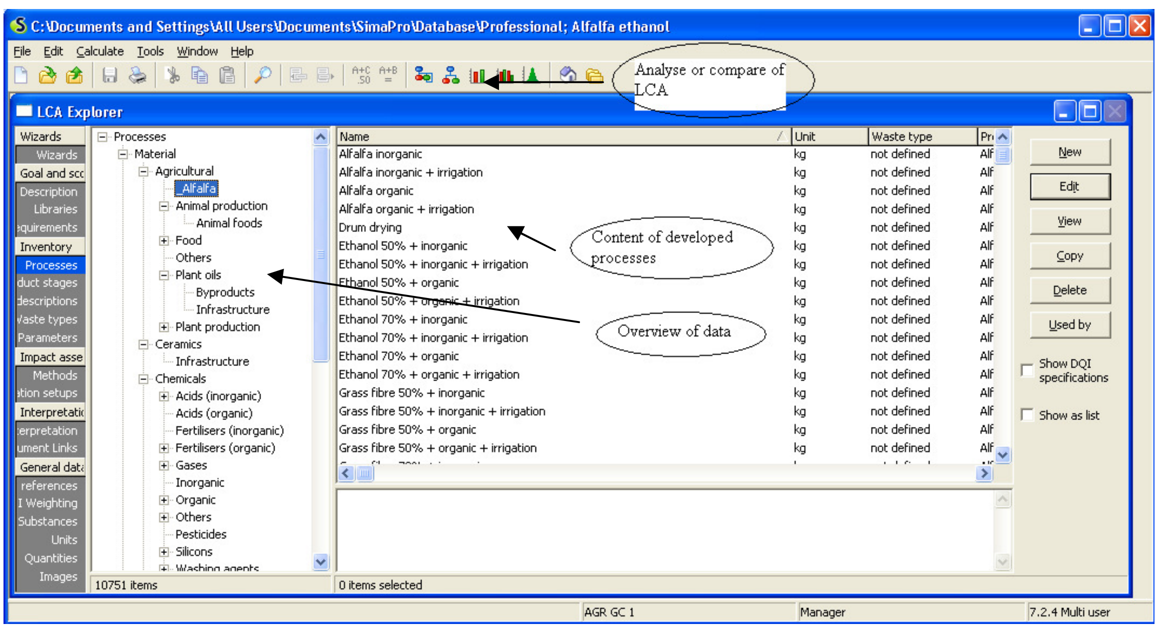


Figure 3.6: Detailed process categories in SimaPro.

Product stages describe the composition of the product, and each product stage refers to processes. Figure 3.7 summarizes the data entering process (input and output data) in SimaPro. The data can include i) environmental data such as raw materials, emissions, non-material emissions and waste; and ii) economic data such as output to the technosphere (one or more products as well as avoided products) and inputs from the technosphere (materials, energy and waste treatment). Processes can be linked to each other to create networks (Figure 3.8). In a network, each process is only represented once, irrespective of the number of times it is used by the other processes. Data can be both foreground and background data. Foreground data are obtained from specific companies or persons. Background data are readily available in databases and literature. These data are distinguished by geographic location, time period of collection, and type of data. SimaPro consists of eleven LCI libraries, notably the following:

- Ecoinvent: 4200 LCA processes for Europe,
- USA input output: 1998 I/O data on 500 commodities,
- Dutch input output: extensive 1999 I/O data on Danish sectors and imports,
- Danish food: recent data on Danish food production,
- Buwal 250: Swiss data for packaging, 1998, and
- ETH- ESU: Energy production for Europe.

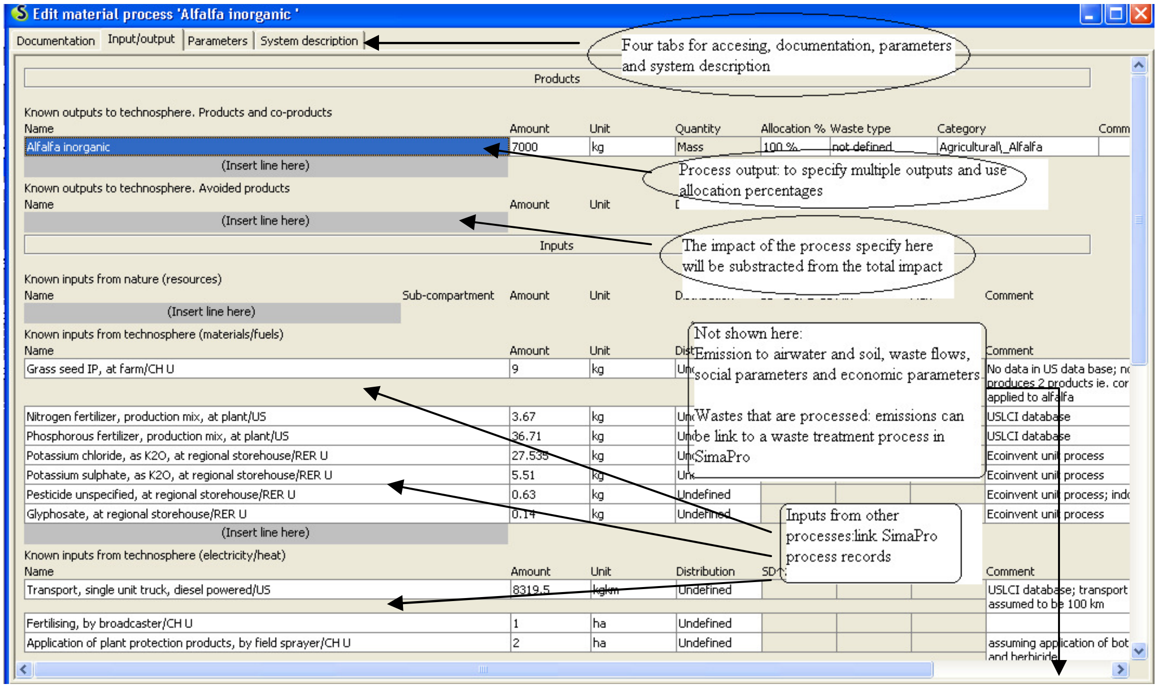


Figure 3.7: Input output window of SimaPro.

By selecting process or product stage, SimaPro generates a graphical representation of the network, where the arrows define flows between processes (Figure 3.8) and the red bar charts indicate the environmental load generated in each process and its upstream processes. The size of the bar chart signifies the contribution to the selected indicator. This inspection enables a researcher to identify the most substantial processes on a given impact category.

Figure 3.9 demonstrates unit and system processes in SimaPro. Data are available as unit processes or systems. Unit processes contain only emissions and resource inputs from one process step and references to input from other unit processes. System processes do not have links to other processes. Unit processes provide a very transparent process tree which enables the contribution of all individual unit processes to be traced. Figure 3.9 illustrates a typical SimaPro window for unit and system processes.

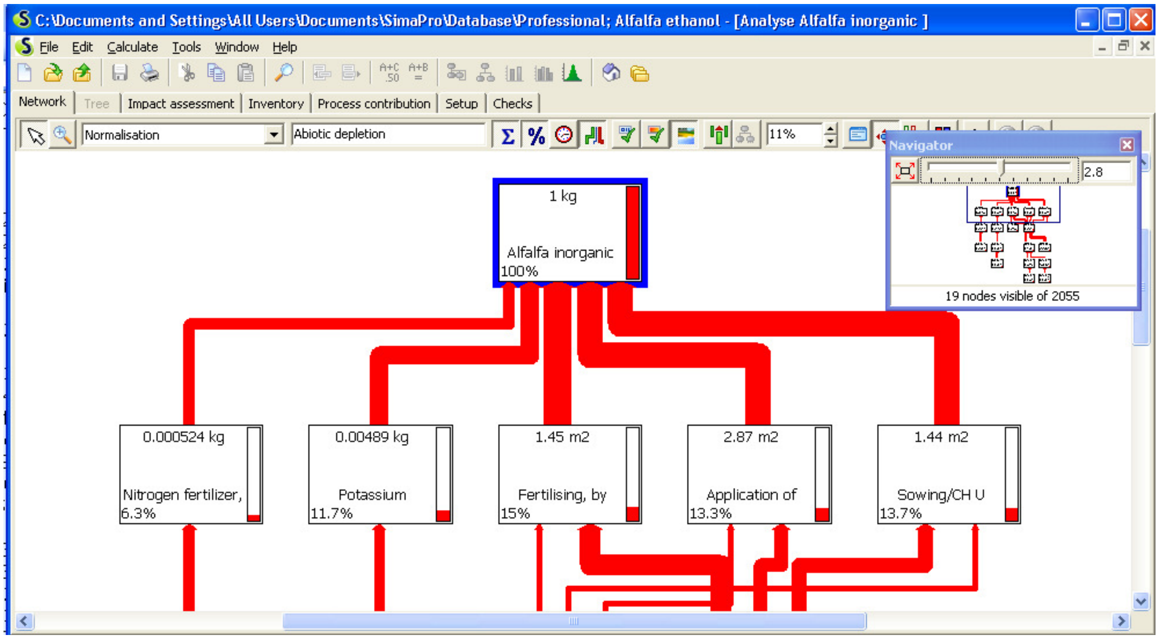


Figure 3.8: Network of processes given as a process tree in SimaPro.

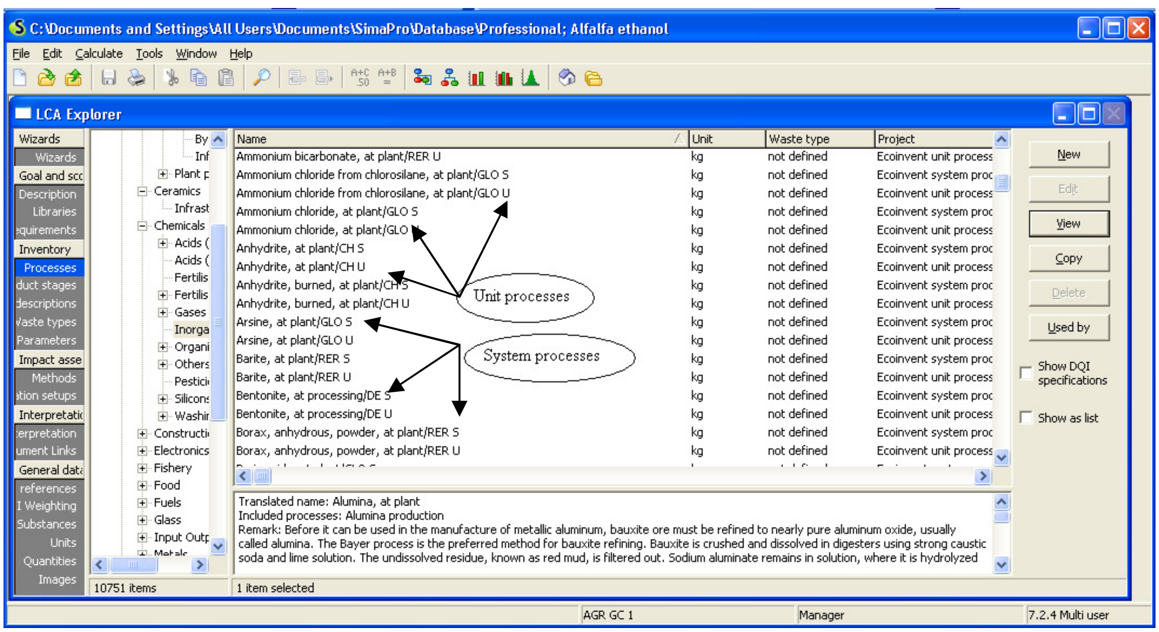


Figure 3.9: Unit versus system processes in SimaPro.

Impact assessment was carried out using CML[1] 2 baseline 2000 V2.05 method. The CML 2 baseline method represents a problem-oriented (midpoint) approach driven by environmental problems (the so-called mid-point of the cause-effect chain) rather than

[1] Centre of Environmental Science, Leiden University, The Netherlands.

by damage (the end-point of this chain) (Guinée et al. 2001). The potential impact categories analysed were abiotic depletion (AD), acidification (A), eutrophication (E), global warming (GW), and human toxicity (HT). Based on the availability of information, the US life cycle inventory (USLCI) database and Ecoinvent were used because they provide relevant agriculture data within SimaPro 7. Ecoinvent provides a broad range of data with a long learning experience (Luo et al. 2009b).

3.5 Inventory analysis

All the data for the study were gathered from different sources and procedures. With data limitations on alfalfa feedstock, it was necessary to adapt data from related studies on feedstocks such as corn stover. Process units were employed where the data were missing, with a justification of all assumptions used. Agricultural field activities (in S1) were characterized by using information from personal communications with alfalfa growers and expert advisors. Alfalfa cultivation data were gathered from research papers and government fact sheets. Because of the lack of data, fertilizer data for irrigated cultivation were used for non-irrigated scenarios as well. Grass seed was used as a proxy for alfalfa seed in the Ecoinvent database (this database does not have an input data line for alfalfa seed). Transportation of all the inputs within the system boundary was based on an average distance of 100 km traveled by a diesel powered single unit truck (USLCI database). Labour use, transportation of personnel, and emissions from fertilizer and machinery are excluded from this subsystem. The scenarios considered were alfalfa cultivation with irrigation vs. without irrigation, and with inorganic fertilizers vs. with organic fertilizers.

Inventory data for the baling and pre-processing subsystem (S2) were collected from the Ecoinvent database. Large round bales weighing around 700 kg were considered in this subsystem. All agricultural processes of this subsystem were selected from Ecoinvent database. It is assumed that alfalfa is swathed and dried on the field before baling.

Regarding the ethanol production subsystem (S3), the conversion of alfalfa stem into ethanol involves pretreatment, hydrolysis and fermentation, followed by distillation. Design parameters and performance data for the production process were adapted from the Galbe and Zacchi (1992) study on wood biomass-based ethanol. Yield data were taken from government reports for Saskatchewan alfalfa cultivation, and some of the assumptions were derived from existing literature.

4. Results and Discussion

This chapter consists of three main subsections. The first subsection includes a summary of mass balance sheets for different scenarios of the ethanol production subsystem (S3). Energy analysis on each subsystem is presented in the second subsection, and LCA results for the three subsystems under different scenarios are presented in subsequent subsections.

4.1 Quantification of inputs and outputs (mass balance approach)

The mass balance of ethanol conversion was calculated for ethanol production subsystem (S3) as discussed in section 3.3.3.5, based on data by Galbe and Zacchi (1992). The mass balance showed variance between amount of water recycling per 1 kg of alfalfa stem biomass processed and per 1 L of ethanol produced. Accordingly, four different detailed mass balance sheets are presented in Appendix A (Tables A.3, A.4, A.5, and A.6). All the calculations were based on dry basis of alfalfa stem biomass. The computations showed that 4.69 kg of alfalfa stem biomass was required to produce 1 L of ethanol. In order to supply this amount of alfalfa biomass, 1.34×10^{-3} ha and 8.53×10^{-3} ha, respectively, of irrigated and non-irrigated alfalfa cultivation were needed. It was apparent that seed, fertilizer, agrochemical, and energy requirements were lower under irrigation relative to non-irrigated cultivation. Table 4.1 provides the spreadsheet summary of mass balance respectively, for processing of 1 kg of alfalfa and production of 1 L of ethanol. It shows the input and final output of S3 for different scenarios. The inputs per kg of biomass were similar for both 50% and 70% water recycling scenarios except for the amount of water for hydrolysis, recycling and waste water. It was apparent that the higher the amount of water recycling, the lower were the amounts of waste water, as well as water added for hydrolysis.

The completed mass balance sheets in the Appendix A (Tables A.3, A.4, A.5, and A.6) consist mainly of pretreatment, SSF, and distillation. During pretreatment, chopped alfalfa and steam were the input while the output was pretreated substrate. Subsequently, the output was subjected to SSF where it underwent several follow up processes. The inputs in SSF were water, pretreated substrate, enzyme, and yeast. Water was added three times: i) to wash the substrate after pretreatment; ii) to adjust the amount of water during hydrolysis; and iii) to wash the output after hydrolysis. Since water recycling was also considered during the process, it was assumed that the recycled water was incorporated during hydrolysis. Therefore, the addition of water during hydrolysis was less than the required amount. Output during SSF was calculated (as discussed in section 3.3.3.2), based on Galbe and Zacchi (1992). The outputs were: i) ethanol from pentose; ii) ethanol from hexose; iii) CO_2 from pentose; iv) CO_2 from hexose; v) acetic acid; vi) glycerol; vii) xylitol; and viii) other solid residue. Fermented slurry was then subjected to distillation as a final step. It was assumed that the fermented slurry consisted of all components of the mass out in SSF, except the gaseous forms (CO_2). During distillation, 95% w/w ethanol was separated from the mixture and other by-products were calculated based on assumptions. Since alfalfa is a protein-rich legume, protein residue was also considered as a byproduct. Chopped alfalfa stem biomass comprised 17.54% protein. It was assumed that 50% of the protein was extracted from solid dry matter (which contained 90% water) during distillation. The rest of the solid material (undigested biomass from fermentation) was considered as fibre residue that was not converted into ethanol. The recycled water was obtained from the stillage (the slurry excluding ethanol and CO_2). Waste water was assumed to be obtained from both stillage and solid residue. Conversion of approximately 6 kg of stem biomass could produce 1 kg of ethanol, 0.9 kg of CO_2, 0.6 kg of protein residue, and 3.9 kg of fibre residue.

Table 4.1: Mass balance calculation for different scenarios in the ethanol conversion subsystem (S3) for processing 1 kg of alfalfa stem feedstock (100% dry matter) or producing 1 L of ethanol (dry mass basis).

	Per kg of alfalfa stem processed		Per litre of ethanol produced	
	Organic/inorganic with 50% water recycling	Organic/inorganic with 70% water recycling	Organic/inorganic with 50% water recycling	Organic/inorganic with 70% water recycling
Mass in	kg	kg	kg	kg
Chopped alfalfa stem	1.00	1.00	4.69	4.69
Steam	0.63	0.63	2.95	2.95
Water for hydrolysis	4.04	2.82	18.91	13.22
Enzyme and yeast	0.33	0.33	1.55	1.55
Recycle water	3.03	4.25	14.22	19.91
Total	9.03	9.03	42.32	42.32
Mass out	kg	kg	kg	kg
Ethanol	0.17	0.17	0.79	0.79
Carbon dioxide	0.16	0.16	0.74	0.74
Protein residue	0.10	0.10	0.46	0.46
Fibre residue	0.66	0.66	3.09	3.09
Waste water	4.91	3.69	23.02	17.33
Recycle water	3.03	4.25	14.22	19.91
Total	9.03	9.03	42.32	42.32

4.2 Energy analysis

This section quantified all energy demands in each scenario and subsystem in terms of materials and processes. The assessments were based on producing 1 kg of alfalfa (S1), processing and baling 1 kg of alfalfa (S2), and ethanol production from 1 kg of stem biomass (S3).

4.2.1 Energy for the cultivation subsystem (S1)

Table 4.2 depicts detailed energy input for the production of 1 kg of alfalfa under different input combinations (scenarios 1, 2, 3, and 4). The energy values contained in inputs for producing alfalfa were the average energy values reported in the literature (Vadas et al. 2008). According to Vadas et al. (2008), energy input values for fertilizers, seed, and agrochemicals were considered as the energy required to produce the items, energy contained in the items, and energy used to transport the items. Energy for seeds was obtained from studies of Vadas et al. (2008) and Patzek (2004). Energy values for nitrogen fertilizer, herbicides, and pesticides were obtained from Vadas et al. (2008), Kim and Dale (2004), and Shapouri et al. (2004). Energy for phosphorous, potassium, and sulfur fertilizers was obtained from studies by Vadas et al. (2008), Patzek (2004), and Kim and Dale (2004). Again, unavailability of adequate data from the literature led to the assumption that energy for sulfur production was similar to potassium fertilizer production, considering potassium sulfate as the fertilizer source. Based on Kim and Dale (2004), it was assumed that energy required to transport alfalfa biomass to the biorefinery was the same as for switchgrass, which was 0.2 MJ/kg (Wang 2001). In addition, transportation of agro chemicals (fertilizers, herbicides, and pesticides) was given as 0.17 MJ of fuel oil and 0.55 MJ of diesel per kilogram of material (Kim and Dale 2004). Energy for manure transportation (in organic scenarios) was adopted from USLCI database, assuming, 14 MJ/kg energy spent for combustion of gasoline in single unit trucks. Irrigation energy was given in two forms, electricity and diesel, amounting respectively 0.862 kJ and 0.157 kJ per 1 L of water irrigated. The rest of the energy data (including manure production and machinery use) were obtained from Ecoinvent database in SimaPro.

According to Table 4.2, the organic scenarios (scenarios 3 and 4) showed higher energy utilization compared to scenarios 1 and 2 because of manure application. This outcome is due to fuel combustion related to massive manure input, transportation and spreading in the field. The highest cumulative energy value was obtained in scenario 3 was 1.305 MJ/kg. However, manure is virtually a waste product for livestock farmers and requires disposal in a proper way. From an economic point of view, the application of this waste product into alfalfa cultivation would be a win-win situation for both livestock farmers and alfalfa cultivators since transportation and handling would be accommodated by both farmers. In other words, the energy expenditure related to manure use by an alfalfa producer can be borne by both the livestock farmer disposing the manure and the alfalfa producer benefitting from the fertilizer value of the manure. However, utilization of manure in corn cultivation is a common practice among livestock farmers. Alfalfa-corn rotation associated with dairy production is popular in North America (Lory 2011) but many producers do not have enough corn farms for all manure produced in livestock farming (Kelling and Schmitt 2011). Therefore, consideration of alternative crops like alfalfa is beneficial for a livestock farmer in a biorefinery

(Daliparthy and Herbert 1996) since the tendency is to apply manure close to its source because of the high cost of transporting manure from one location to another. For instance, Pound-Maker, an ethanol plant in Lanigan, SK is operated by local wheat growers while the co-products of the plant (dried distillers grains with soluble-DDGS) are transferred to the feedlot. On the other hand, integration of livestock manure into alfalfa cultivation would provide benefit to both production processes as a whole in the biorefinery.

Comparing the values in Tables 4.2 demonstrates that the cumulative energy for 1 kg of alfalfa production was comparatively higher for non-irrigated scenarios than for irrigated scenarios. The higher yield in irrigated scenarios outweighs part of the energy spent during production and showed lower energy consumption compared to non-irrigated scenarios. This difference can be observed when comparing the total energy from scenario 1 with scenario 2 and scenario 3 with scenario 4. The observed difference in energy use directly affected the final LCA environmental impact assessment results as well (section 4.3.1).

The results for energy analysis in S1 showed that the least energy requirement was obtained from scenario 2, thus providing the least environmental burden in terms of LCA analysis (section 4.3.1). Therefore, the higher the energy use, the higher would be the environmental burden.

Table 4.2: Energy input in different scenarios of the cultivation subsystem (S1) for 1 kg of alfalfa (leaf and stem) harvested.

Inputs	Energy (MJ)			
	Inorganic + non irrigation	Inorganic + irrigation	Organic + non irrigation	Organic + irrigation
Seeds	0.134	0.085	0.134	0.085
N	0.025	0.016	-	-
P	0.062	0.040	-	-
K	0.031	0.020	-	-
S	0.006	0.004	-	-
Manure	-	-	0.323	0.205
Herbicide	0.006	0.004	0.006	0.004
Pesticide	0.029	0.018	0.029	0.018
Transport alfalfa	0.200	0.200	0.200	0.200
Transport agrochemicals	0.008	0.005	0.000	0.000
Transport manure	-	-	0.372	0.237
Hydraulic loader and spreader	-	-	0.153	0.098
Broadcaster	0.038	0.024	-	-
Field sprayer	0.025	0.016	0.025	0.016
Seeding	0.027	0.017	0.027	0.017
Swathing	0.021	0.013	0.021	0.013
Haying	0.014	0.009	0.014	0.009
Irrigation	-	0.041	-	0.041
Total	0.626	0.512	1.304	0.943

According to Pimentel and Patzek (2005), the average energy input per hectare for producing switchgrass was only about 15.9 x 10^3 MJ per year (3.8 million kcal per year), which was substantially higher than that for alfalfa production. Since alfalfa is a leguminous crop, energy expenditure from inputs is very low. Kim and Dale (2004) reported the cumulative energy for producing biomass of seven states in United States, summarized in Table 4.3. Case "A" indicates that carbon dioxide is a by-product of ammonia manufacture; case "B" indicates that carbon dioxide is a waste in the ammonia production process. Comparing Tables 4.2 and 4.3, the literature results are within the range of calculated total energy in this study.

Table 4.3: Cumulative energy for 1 kg of crop production (Kim and Dale 2004).

Crop	Cumulative energy value (MJ)	
	Case A*	Case B
Corn	1.99	2.66
Soybean	1.98	2.04
Alfalfa	1.24	1.24
Switchgrass	0.97	1.34

*Table 4.3 contains two cumulative energy values for nitrogen fertilizer production: One is for the case in which carbon dioxide produced in the ammonia plant is regarded as an emission (i.e., a *waste*), denoted by "nitrogen fertilizer B"; the other value, denoted by "nitrogen fertilizer A," is the result considering the carbon dioxide generated in the ammonia plant as a co-product.

4.2.2 Energy for the baling and pre-processing subsystem (S2)

Energy for each process step at pre-processing and baling was calculated for each scenario in this subsystem. All the process steps for each scenario were similar in this subsystem and the deviation of total energy in S1 and S2 was due to the energy deviation from S1. The process units were baling, bale loading, transporting, tub grinding, and drum drying. All the energy data except transportation were obtained from Ecoinvent database, while transportation energy was adopted from USLCI database. Table 4.4

provides accumulated energy values for each scenario in S2. The difference in the total energy values is related to the different input combinations used in S1. It was apparent that the irrigated scenarios had lower energy requirements relative to non-irrigated scenarios. Drying energy (from drum drying) was twofold: from electricity and from heat, according to the Ecoinvent database. It was the most energy consuming process in S2, with approximately 0.197 MJ in electricity and heat demand per 1 kg of biomass. To calculate the total energy in this subsystem, energy spent on S1 for each scenario was added to the four scenarios in S2. The highest energy consumption was observed in scenario 3 (stem + organic fertilizer + non-irrigation) which was 1.62 MJ/kg. Kumar and Sokhansanj (2007) reported that energy consumption for making a dry kg of square bales and round bales using switchgrass biomass was 0.200 MJ and 0.236 MJ, respectively lower than the values calculated in this study for alfalfa biomass (0.312 MJ/kg). The process steps included were swathing, raking, baling, road-siding, staking, and tarping. Adler et al. (2007) reported energy consumption for alfalfa baling as 0.045 MJ/kg.

Compared to the calculated energy values, the aforementioned values illustrate some deviations since energy expenditure is associated with the given operation system and energy source. For instance, the baling process considered in this study related to the production of large round bales, whereas Kumar and Sokhansanj (2007) studied the production of large square bales. Since machinery and processes could vary depending on the study, energy output could also have some deviations.

Table 4.4: Energy input in the baling and pre-processing subsystem (S2) for 1 kg alfalfa (leaf and stem).

Processes	Energy (MJ)			
	Stem + inorganic + no irrigation	Stem + inorganic + irrigation	Stem + organic + no irrigation	Stem + organic+ no irrigation
Energy from S1	0.626	0.512	1.305	0.944
Baling	0.053	0.053	0.053	0.053
Loading	0.006	0.006	0.006	0.006
Transporting	0.003	0.003	0.003	0.003
Tub grinding	0.054	0.054	0.054	0.054
Drum drying	0.197	0.197	0.197	0.197
Energy input for 1 kg of alfalfa processed in S2 (MJ)	0.313	0.313	0.313	0.313
Total energy input for 1 kg of alfalfa processed including S1 (MJ)	0.939	0.825	1.618	1.257

4.2.3 Energy for the ethanol production subsystem (S3)

Tables 4.5 and 4.6 present accumulated energy values of processing 1 kg alfalfa stem into ethanol with each process step at 50% and 70% of water recycling, respectively for different scenarios. Tables 4.7 and 4.8 depict the energy values in each scenario associated with 1 L of ethanol production at 50% and 70% of water recycling, respectively. Unit energy values for each process step in S3 were obtained from Ecoinvent database except for ethanol plant heating values. With the scarcity of data, hydrolysis and fermentation energy could not be separately distinguished; instead, a cumulative value was generated by using the energy values for corn stover to ethanol conversion given in Table 3.4. Using the values in Table 3.4, ethanol plant heat value was generated in Tables 4.5, 4.6, 4.7 and 4.8 and represented as an average, minimum and maximum value of ethanol plant heat. The energy for steam was twofold, namely energy from natural gas and from heavy fuel oil. It was given in Ecoinvent database that natural gas and heavy fuel oil were burned in the furnace during steam generation. Since there were no chemicals used in the pretreatment process, it was assumed that steam energy was similar to energy consumption at the pretreatment (steam explosion) stage. The energy for enzyme and yeast was assumed to be similar to the energy available in yeast paste. There were three types of energy associated with enzyme and yeast production: electricity, heat from biogas, and heat from natural gas since it was a combination of multiple processes. Electricity was needed to pump water to the plant, and it was depicted as tap water pumping energy in Tables 4.5, 4.6, 4.7, and. 4.8.

Table 4.5: Energy input in the ethanol production subsystem (S3) and the whole system (S1, S2, and S3) at 50% water recycling using 1 kg of alfalfa stem processed. S1 is alfalfa cultivation subsystem, S2 is baling and pre-processing subsystem, and S3 is ethanol conversion subsystem.

Processes	Energy (MJ/kg)			
	Inorganic + non-irrigated	Inorganic + Irrigated	Organic + non-irrigated	Organic + irrigated
Energy from S1 and S2	0.94	0.82	1.62	1.26
Steam generation	1.79	1.79	1.79	1.79
Tap water pumping	0.00	0.00	0.00	0.00
Enzyme and yeast production	2.41	2.41	2.41	2.41
Ethanol plant_ Heat (Average)	2.79	2.79	2.79	2.79
Ethanol plant_ Heat (Maximum)	4.00	4.00	4.00	4.00
Ethanol plant_ Heat (Minimum)	1.78	1.78	1.78	1.78
Standard deviation	0.62	0.62	0.62	0.62
Total Energy (Average) for S3 only	6.99	6.99	6.99	6.99
Total Energy (Maximum) for S3 only	8.20	8.20	8.20	8.20
Total Energy (Minimum) for S3 only	5.99	5.99	5.99	5.99
Standard deviation for S3 only	0.62	0.62	0.62	0.62
Total Energy (Average) for S1, S2, and S3	7.93	7.82	8.61	8.25
Total Energy (Maximum) for S1, S2, and S3	9.14	9.03	9.82	9.46
Total Energy (Minimum) for S1, S2, and S3	6.92	6.81	7.60	7.24
Standard deviation for S1, S2, and S3	0.62	0.62	0.62	0.62

Table 4.6: Energy input in the ethanol production subsystem (S3) and the whole system (S1, S2, and S3) at 70% water recycling using 1 kg of alfalfa stem processed. S1 is alfalfa cultivation subsystem, S2 is baling and pre-processing subsystem, and S3 is ethanol conversion subsystem.

Processes	Energy (MJ/kg)			
	Inorganic + non irrigation	Inorganic + irrigation	Organic + non irrigation	Organic + irrigation
Energy for S1 and S2	0.94	0.82	1.62	1.26
Steam generation	1.79	1.79	1.79	1.79
Tap water pumping	0.00	0.00	0.00	0.00
Enzyme and yeast production	2.41	2.41	2.41	2.41
Ethanol plant_ Heat (Average)	3.21	3.21	3.21	3.21
Ethanol plant_ Heat (Maximum)	4.60	4.60	4.60	4.60
Ethanol plant_ Heat (Minimum)	2.05	2.05	2.05	2.05
Standard deviation	0.71	0.71	0.71	0.71
Total Energy (Average) for S3 only	7.41	7.41	7.41	7.41
Total Energy (Maximum) for S3 only	8.80	8.80	8.80	8.80
Total Energy (Minimum) for S3 only	6.25	6.25	6.25	6.25
Standard deviation for S3 only	0.71	0.71	0.71	0.71
Total Energy (Average) for S1, S2, and S3	8.35	8.23	9.03	8.67
Total Energy (Maximum) for S1, S2, and S3	9.74	9.62	10.42	10.06
Total Energy (Minimum) for S1, S2, and S3	7.19	7.07	7.87	7.51
Standard deviation for S1, S2, and S3	0.71	0.71	0.71	0.71

Table 4.7: Energy input in the ethanol production subsystem (S3) and the whole system (S1, S2, and S3) at 50% water recycling for 1 L of ethanol produced. S1 is alfalfa cultivation subsystem, S2 is baling and pre-processing subsystem, and S3 is ethanol conversion subsystem.

Processes	Inorganic + non irrigation	Inorganic + irrigation	Organic + non irrigation	Organic + irrigation
Energy from S1 and S2	4.40	3.87	7.59	5.89
Steam generation (MJ)	8.39	8.39	8.39	8.39
Tap water pumping (MJ)	0.02	0.02	0.02	0.02
Enzyme and yeast (MJ)	11.29	11.29	11.29	11.29
Ethanol plant_ Heat (Average) (MJ)	13.10	13.10	13.10	13.10
Ethanol plant_ Heat (Maximum) (MJ)	18.76	18.76	18.76	18.76
Ethanol plant_ Heat (Minimum) (MJ)	8.37	8.37	8.37	8.37
Standard deviation (MJ)	2.90	2.90	2.90	2.90
Total Energy (Average (MJ)) for S3	32.78	32.78	32.78	32.78
Total Energy (Maximum (MJ)) for S3	38.43	38.43	38.43	38.43
Total Energy (Minimum (MJ)) for S3	28.05	28.05	28.05	28.05
Standard deviation (MJ) for S3	3.29	3.29	3.29	3.29
Total Energy (Average (MJ)) for S1, S2, and S3	37.18	36.65	40.37	38.67
Total Energy (Maximum (MJ)) for S1, S2, and S3	42.83	42.30	46.02	44.32
Total Energy (Minimum (MJ)) for S1, S2, and S3	32.45	31.92	35.64	33.94
Standard deviation (MJ) for S1, S2, and S3	3.29	3.29	3.29	3.29

Note: The values were generated by dividing per hectare energy by the ethanol yield (1174 L for irrigated and 747 L for non- irrigated scenarios).

Table 4.8: Energy input in ethanol production subsystem (S3) and the whole system (S1, S2, and S3) at 70% water recycling for 1 L of ethanol produced. S1 is alfalfa cultivation subsystem, S2 is baling and pre-processing subsystem, and S3 is ethanol conversion subsystem.

Processes	Inorganic + non irrigation	Inorganic + irrigation	Organic + non irrigation	Organic + irrigation
Energy from S1 and S2	4.40	3.87	7.59	5.89
Steam generation (MJ)	8.39	8.39	8.39	8.39
Tap water pumping (MJ)	0.02	0.02	0.02	0.02
Enzyme and yeast (MJ)	11.29	11.29	11.29	11.29
Ethanol plant_ Heat (Average) (MJ)	15.06	15.06	15.06	15.06
Ethanol plant_ Heat (Maximum) (MJ)	21.58	21.58	21.58	21.58
Ethanol plant_ Heat (Minimum) (MJ)	9.62	9.62	9.62	9.62
Standard deviation (MJ)	3.34	3.34	3.34	3.34
Total Energy (Average (MJ)) for S3	34.76	34.76	34.76	34.76
Total Energy (Maximum (MJ)) for S3	41.28	41.28	41.28	41.28
Total Energy (Minimum (MJ)) for S3	29.32	29.32	29.32	29.32
Standard deviation (MJ) for S3	3.34	3.34	3.34	3.34
Total Energy (Average (MJ)) for S1, S2, and S3	39.16	38.63	42.35	40.65
Total Energy (Maximum (MJ)) for S1, S2, and S3	45.68	45.15	48.87	47.17
Total Energy (Minimum (MJ)) for S1, S2, and S3	33.72	33.19	36.91	35.21
Standard deviation (MJ) for S1, S2, and S3	3.34	3.34	3.34	3.34

Note: The values were generated by dividing per hectare energy by the ethanol yield (1174 L for irrigated and 747 L for non- irrigated scenarios).

Tables 4.5, 4.6, 4.7, and 4.8 indicate that the total energy for a given scenario was higher at 70% water recycling compared to energy at 50% water recycling. It is apparent that the irrigated scenarios had lower energy consumption in comparison to non-irrigated scenarios, suggesting a correlation between energy consumption and the higher alfalfa yield (and hence high stem biomass processed) in irrigated scenarios. The results of environmental impact assessment (section 4.3) also show this correlation with respect to energy consumption. Throughout the life cycle of ethanol production (from cradle-to-gate analysis), scenario 2 consumed an average of 7.82 MJ/kg of energy at 50% water recycling; this scenario represented the least energy utilization and the best choice among the other scenarios.

Statistical analysis (using SPSS 14.0 for Windows: 2005, LEAD Technologies, Inc.) was carried out to determine the significance between average total energy for each scenarios in Tables 4.5, 4.6, 4.7, and 4.8 and the results are given in Appendices B, C, D, and E respectively. The amount of variance in the total energy input that can be explained by the model is represented by the coefficient of determination (R^2). In all outputs of ANOVA given in Appendices B, C, D, and E, the model explained respectively around 15%, 10%, 21%, and 20% of the variance and predictive accuracy. The ANOVA summary table in Appendix B revealed that the between-scenario mean square (the variation explained by the model) was 1.268 (3.803/3), and the within-scenario mean square (the variation unexplained) was 0.383 (13.77/36). The F-ratio was 3.314 (1.268/ 0.383), and the p-value < 0.05, indicating that the mean energy input of the four scenarios was significantly different. Similarly in Appendices C, D and E, the p- value < 0.05 showed that the mean energy input of the four scenarios was significantly different. The post-hoc tests of LSD (Least Significant Difference) of Appendices B and C showed that the average total energy input for processing 1 kg of alfalfa stem biomass in scenario 1 was not significantly different from scenario 2 and 4 but significantly different from scenario 3. The average total energy input in scenario 2 was not significantly different from scenario 1 and 4. Thus, the energy input in scenario 3 (inorganic, non-irrigated alfalfa cultivation) was statistically the highest among the four scenarios in this study. The post-hoc tests (LSD) of Appendices D and E showed that the average total energy input for producing 1 L of ethanol in scenario 1 was not significantly different from scenario 2 but significantly different from scenario 3 and 4. The average total energy input in scenario 2 was not significantly different from scenario 1 but scenario 3 and 4. Therefore, the organic scenarios (scenario 3 and 4) had significantly higher energy input than the inorganic scenarios (scenario 1 and 2).

The total energy values for only S3 in Tables 4.7 and 4.8 was compared with values reported in the previous studies. Pimentel and Patzek (2005) reported the total energy consumption of producing 1 L of ethanol from switchgrass and wood cellulose as 31.19 MJ and 37.66 MJ respectively. Compared to these values, ethanol from alfalfa stem biomass appears to consume comparatively higher energy. The unit energy expenditure showed inorganic irrigated scenario as the favourable input combination in S3 at both water recycling scenarios.

Since this study was based on research data and assumptions (from SimaPro databases and other studies), the energy values would not totally represent the exact energy consumption of the system. Errors in the estimates can be minimized by incorporating actual data into the system instead of making assumptions on process steps.

However, a sensitivity analysis on LCA results has been conducted to quantify the variation of output results due to ethanol plant energy input.

Further, Pimentel and Patzek (2005) reported that 1 L of ethanol contains 21.46 MJ and illustrated that both switchgrass and wood biomass required more energy to produce 1 L of ethanol. Similarly, S3 system required more energy to produce ethanol than it contains. However if the byproduct credits are incorporated into the calculation, the system would generate a positive energy balance.

Comparing the three subsystems S1, S2, and S3 shows that alfalfa production subsystem (S1) consumed around 6.2% to 15.1% of total energy. This amount was significantly lower compared to the other studies. Since alfalfa is a leguminous crop, it consumes fewer inputs during cultivation, unlike non-leguminous crops. For instance, studies by Shapouri et al. (2002), Wang (2001), Pimentel (1991), Sheehan (1998), and Kim and Dale (2004) showed that agricultural production processes accounted for 27% to 44% of total energy consumption in producing bio-based products. The ethanol conversion subsystem (S3) was the highest energy consuming subsystem in this study, consuming 77.5% to 94.8% of total energy in all the scenarios analyzed. In order to increase efficiency and productivity, appropriate measures are required in modifying S3 for the alfalfa-to-ethanol life cycle analysis. The highest contribution arose from ethanol plant heating process (shown in detail in Figure 4.19). By incorporating co-products such as lignin for heat generation, energy input can be minimized. In addition, other process steps such as pretreatment and enzyme and yeast production can be modified in a favourable manner to reduce the impact. Overall, the least energy consuming subsystem was baling and pre-processing, with a 3.5- 4.0% contribution to the total energy input.

4.3 Life cycle assessment

All the data used in the LCA are as described in sections 3.3 and 4.1. SimaPro 7.2.4 Professional multi-user software was used to analyze the impact of each subsystem on abiotic depletion (AD), acidification (A), eutrophication (E), global warming (GW), and human toxicity (HT), using CML 2 baseline 2000 V2.05 / World, 1990 method (EarthShift 2011). Special attention was paid to greenhouse gas emissions, which are a factor in global warming. Global warming is the contribution of processes or materials in terms of equivalent CO_2 per functional unit.

In the results, abiotic depletion is given as equivalent kilograms of an extracted element (kg antimony equivalent) or extracted mineral. Acidification is expressed as equivalent SO_2 emission per functional unit. Equivalent PO_4^{3-} emissions per functional unit is represented in eutrophication. For each toxic substance, human toxicity is expressed as 1, 4-dichlorobenzene equivalents per kg of emission (SimaPro 7 2003).

4.3.1 Environmental impact performance of cultivation subsystem (S1)

The different input combinations (irrigated or non-irrigated, organic or inorganic) were considered in this subsystem to determine the input combination with the least environmental burdens. The scenarios were based on i) whether the cultivation was irrigated or non-irrigated; and ii) whether organic fertilizer or inorganic fertilizer was used. Therefore, there were four different input combinations for this subsystem.

According to the characterization results (per kg of alfalfa produced) under the aforementioned scenarios, GW impact category was significantly different for all four scenarios, while the other impact categories did not show comparatively high deviation in their results (Table A.1). Changes in the environmental impact represent the effect of changing the input under each scenario. The results revealed AD, A, GW, and HT impact for inorganic scenarios were lower compared to organic scenarios. The environmental impact of AD, A, E, GW, and HT are presented in the following sections.

4.3.1.1 Abiotic depletion

According to Figure 4.1, scenarios with organic fertilizers had slight increases in the environmental impact (AD results) compared to scenarios with inorganic fertilizers.

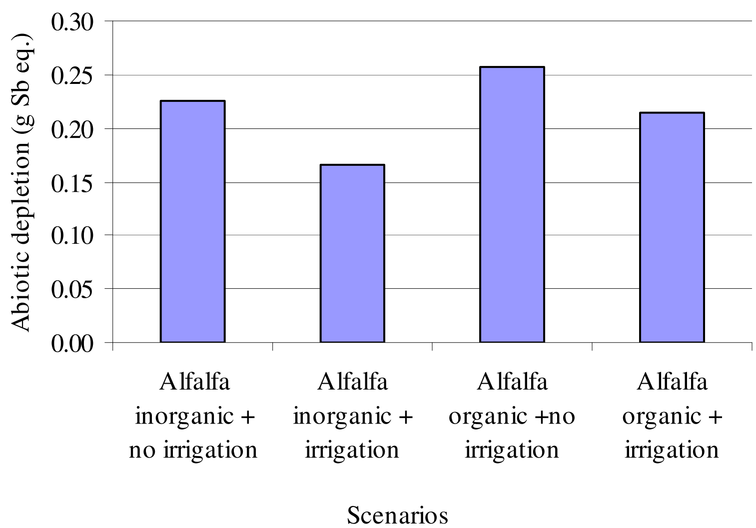


Figure 4.1: LCA characterization results for abiotic depletion based on 1 kg of alfalfa cultivation in cultivation subsystem (S1) under various scenarios.

Abiotic depletion (AD) was affected mainly by the use of non-renewable energy sources such as coal, natural gas, and crude oil. The effects of AD were associated with agricultural machinery needed for each processing step. The bulky nature of organic fertilizer consumed considerably more machinery time for manure application. In addition, scenarios with irrigation showed lower impact compared to the scenarios without irrigation since unit energy spent for alfalfa was lesser in irrigated scenarios than non-irrigated scenarios.

4.3.1.2 Acidification

Figure 4.2 depicts considerable differences in acidification in each scenario. Scenarios with organic fertilizers showed comparatively higher impact compared to scenarios with inorganic fertilizers.

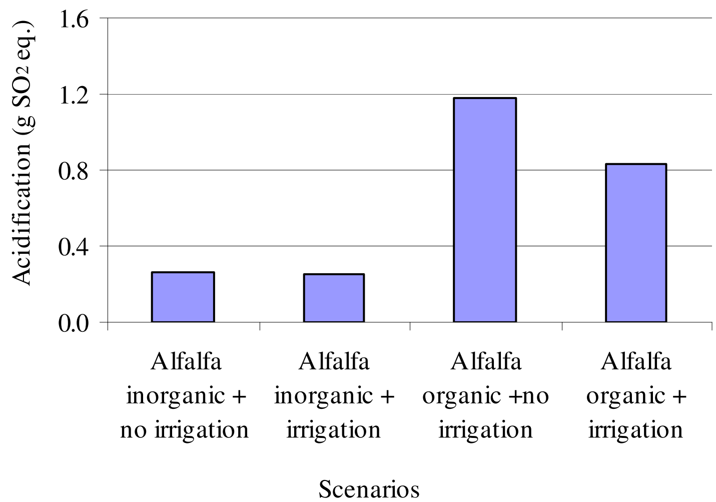


Figure 4.2: LCA characterization results for acidification based on 1 kg of alfalfa cultivation in cultivation subsystem (S1) under various scenarios.

Acidification was mainly contributed by manure use (Figure 4.3). The mass of manure was significantly higher in organic scenarios compared to the mass involved for inorganic fertilizer application, resulting in higher environmental burdens from organic fertilizer scenarios. Garcia et al. (2009b) reported that acidification was mainly affected by SO_2 emissions from P-based fertilizers and NO_x emissions from agricultural machinery use. Figure 4.3 further illustrates process contribution of organic scenarios with and without irrigation. Apparently, the use of manure had the highest contribution for acidification in organic production scenarios.

Similarly, the relative contribution of processes for two inorganic scenarios is illustrated in Figure 4.4. Phosphorous fertilizer application was the major contributor to acidification in inorganic scenarios, whereas the other operations had relatively low contributions. In fact, the addition of irrigation reduced the impact from each process contributor in inorganic scenarios. In both figures 4.3 and 4.4, 5% cut-off setting was used so that, processes those contribute more than 5% are included in the graphs.

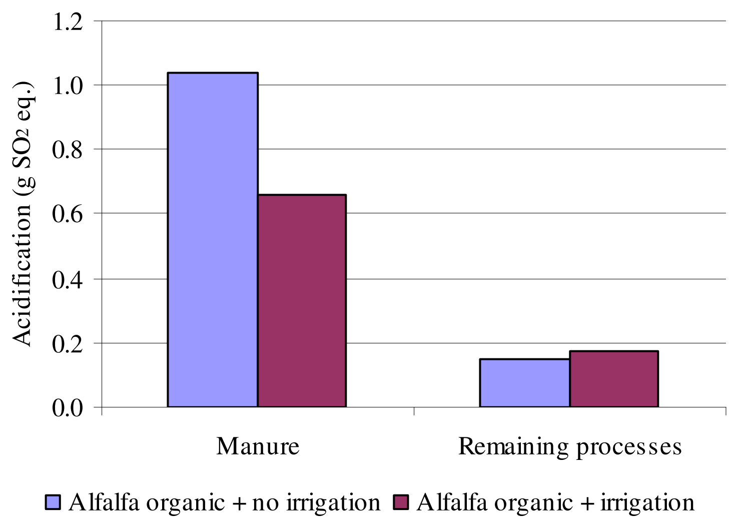


Figure 4.3: Process contribution of alfalfa cultivation subsystem (S1) in organic scenarios at 5% cut-off for acidification (scenarios 3 and 4).

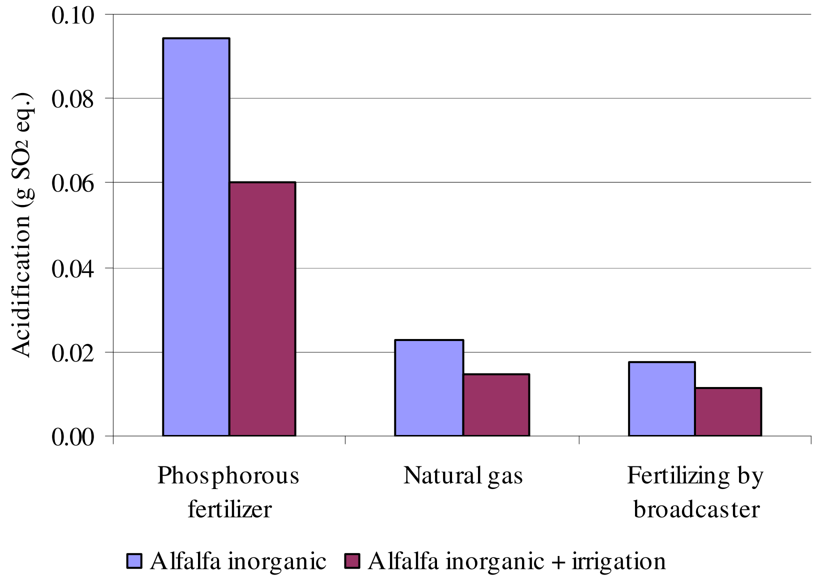


Figure 4.4 : Process contribution of alfalfa cultivation subsystem (S1) in inorganic scenarios at 5% cut-off for acidification (scenarios 1 and 2).

4.3.1.3 Eutrophication

Eutrophication was mainly caused by fertilizer use. Garcia et al. (2009b) reported that N_2O emission derived from agricultural machinery use and fertilizer production; SO_2 emissions from P-fertilizers were the major process contributors to eutrophication. Thus, ammonia, nitrogen oxide, phosphate, and nitrate became the major compounds of concern. According to Figure 4.5, inorganic production scenarios showed higher impact on eutrophication while the organic production scenarios had a lower impact. In addition, irrigation scenarios had lower impacts compared to non-irrigated scenarios.

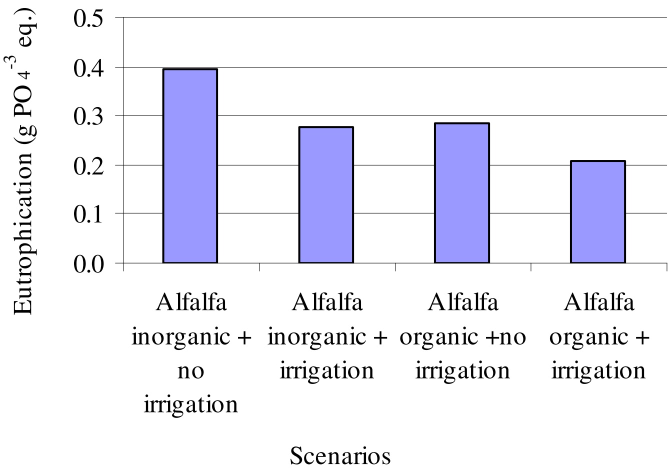


Figure 4.5: LCA characterization results for eutrophication based on 1 kg of alfalfa cultivation in cultivation subsystem (S1) under various scenarios.

For inorganic scenarios, phosphorus fertilizer application contributed mainly to eutrophication, whereas for organic fertilizer scenarios, compost was the major contributor (Figures 4.6 and 4.7 respectively). Figures 4.6 and 4.7 were generated with processes that have contributed more than 5% to the acidification.

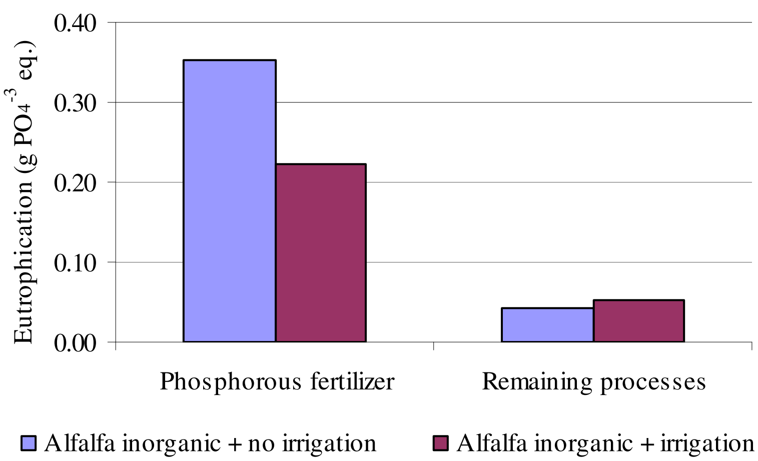


Figure 4.6: Process contribution of alfalfa cultivation subsystem (S1) in inorganic scenarios at 5% cut-off for eutrophication (scenarios 1 and 2).

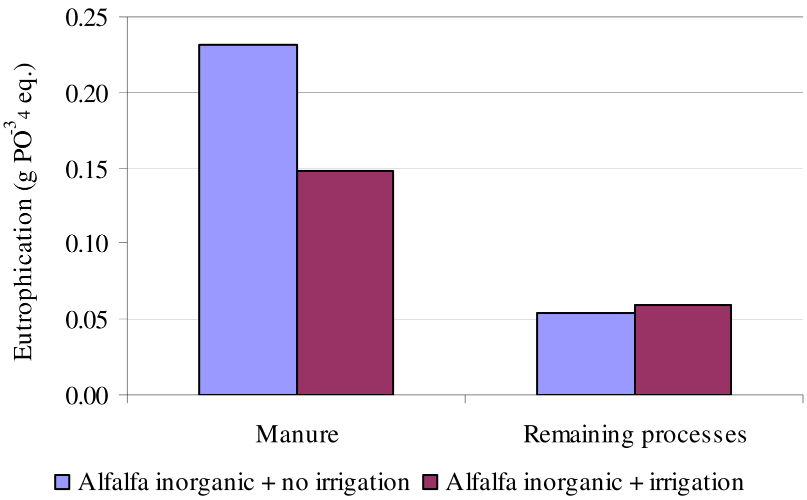


Figure 4.7: Process contribution of alfalfa cultivation subsystem (S1) in organic scenarios at 5% cut-off for eutrophication (scenarios 3 and 4).

Eutrophication results for organic fertilizer scenarios were slightly lower because the nutrient released from compost was slower than the direct application of inorganic nutrients. It is also apparent that with irrigation, the impact of fertilization is reduced in terms of eutrophication, since irrigation tends to dilute the fertilizer.

4.3.1.4 Global warming potential

According to Figure 4.8, the minimum environmental burden in alfalfa cultivation was obtained for global warming by the combination of inorganic fertilizers with irrigation. Global warming, an extremely important issue, is frequently discussed on the national or global scale. The three main global warming gases (carbon dioxide, dinitrogen monoxide, and methane) are seen as contributing to an increase in global warming (Table 4.9). Carbon dioxide is emitted mainly from fossil fuel combustion in machinery during land preparation, transportation, and other agricultural activities. Dinitrogen monoxide is mainly from N based fertilizer application. In inorganic scenarios, machinery use (e.g. seeding, spraying etc.) had the highest impact on global warming, while the manure affected GW significantly in organic scenarios (Figure 4.9).

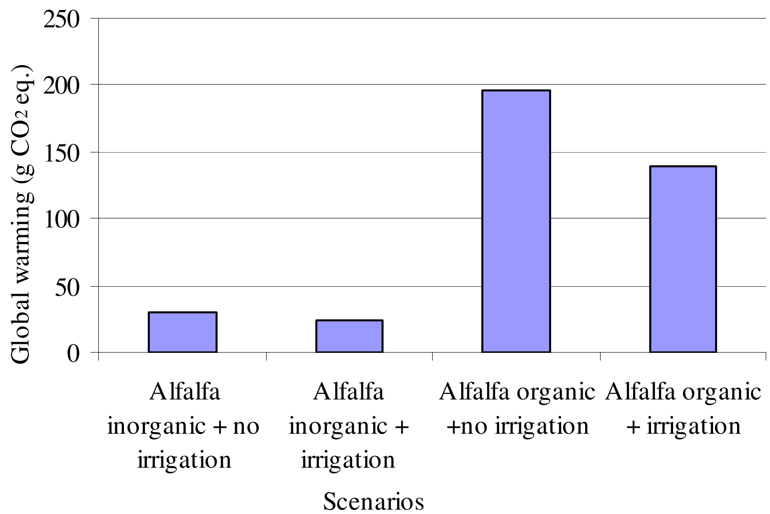


Figure 4.8: LCA characterization results for global warming based on 1 kg of alfalfa cultivation in cultivation subsystem (S1) under various scenarios.

Table 4.9: Contribution of greenhouse gas emissions based on inventory analysis for 1 kg of alfalfa production in S1 at 10% cut-off.

Substance (kg CO_2 eq.)	Alfalfa inorganic + no irrigation	Alfalfa inorganic + irrigation	Alfalfa organic + no irrigation	Alfalfa organic + irrigation
Carbon dioxide	0.026	0.020	0.031	0.028
Dinitrogen monoxide	0.001	0.002	0.032	0.049
Methane	0.000	0.000	0.117	0.074
Remaining substances	0.002	0.001	0.002	0.001

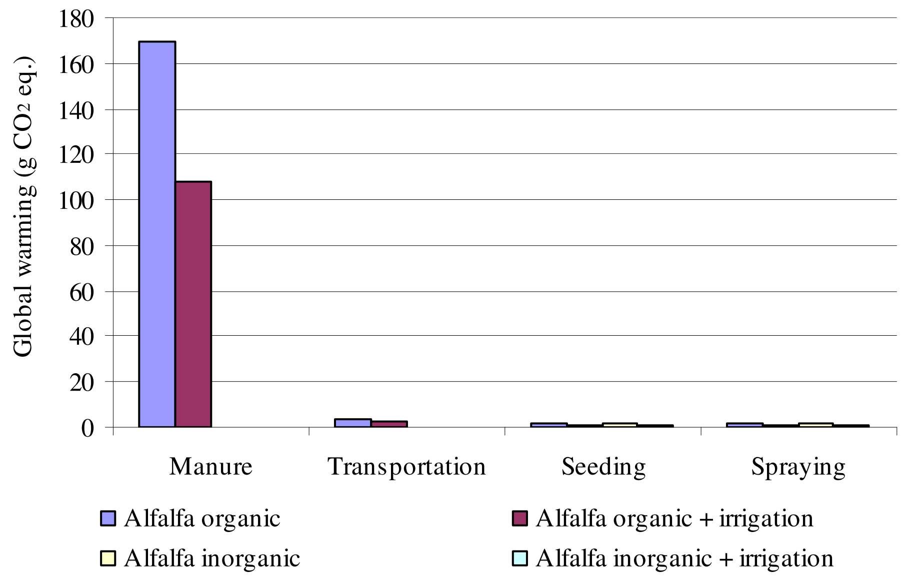


Figure 4.9: Process contribution at 2% cut-off for global warming (kg CO_2 eq.) under various scenarios in alfalfa cultivation subsystem (S1).

Employing organic fertilizers (compost) increased greenhouse gases in comparison to inorganic fertilizer use because it was applied in large amounts. Besides, alfalfa as a legume required very low nitrogen fertilizer input quantities, thereby significantly reducing GHG emission in inorganic scenarios. Irrigated cultivation had lower GHG emission compared to non-irrigated scenarios as per functional unit. Since irrigated fields provided higher yields than non-irrigated fields, this helped to mitigate GHG emissions by sequestrating a huge amount of CO_2 into the environment during plant growth. It was sufficient to compensate for the amount of extra GHG emitted by machinery operations during irrigation. Therefore, irrigated scenarios show lower environmental burdens than those created by non-irrigated scenarios. The study by Garcia et al. (2009b) showed similar results for E10 and E85 fuel blends using Ethiopian mustard (*Brassica carinata*). In fact, the higher the amount of ethanol in the blend (use of more biomass), the higher the CO_2 uptake during the growing of the biomass, which offsets CO_2 derived from agricultural machinery (Garcia et al. 2009b).

4.3.1.5 Human toxicity

Results for human toxicity showed considerable deviation in the four scenarios (Figure 4.10). Irrigated scenarios showed lower burdens compared to the non-irrigated scenarios. Human toxicity impacts resulted mainly from machinery production, since it requires metals such as iron and copper. The emission of hazardous elements such as polycyclic aromatic hydrocarbons, chromium, arsenic, selenium, barium, etc., by those processes adversely affect to the human health. Figure 4.11 displays the magnitude of the effect from each process on HT.

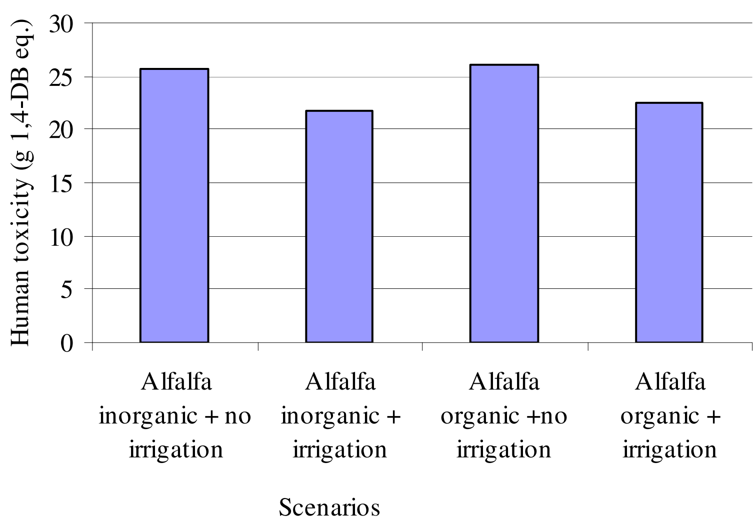


Figure 4.10: LCA characterization results for human toxicity based on 1 kg of alfalfa cultivation in cultivation subsystem (S1) under different scenarios.

Ferrochromium is an alloy composed of chromium and iron and is consumed in steel production; it is the main contributor to human toxicity in all four scenarios. Ferrochromium disposal and copper are associated with machinery production and have a major impact on human health. In addition, gasoline production contributes to the higher index value in HT because of the combustion of gasoline in machinery operation (Kadam 2002). It was apparent that for the irrigated scenarios, the magnitude of the impact was lower even though irrigation equipment became an additional contributor to the system.

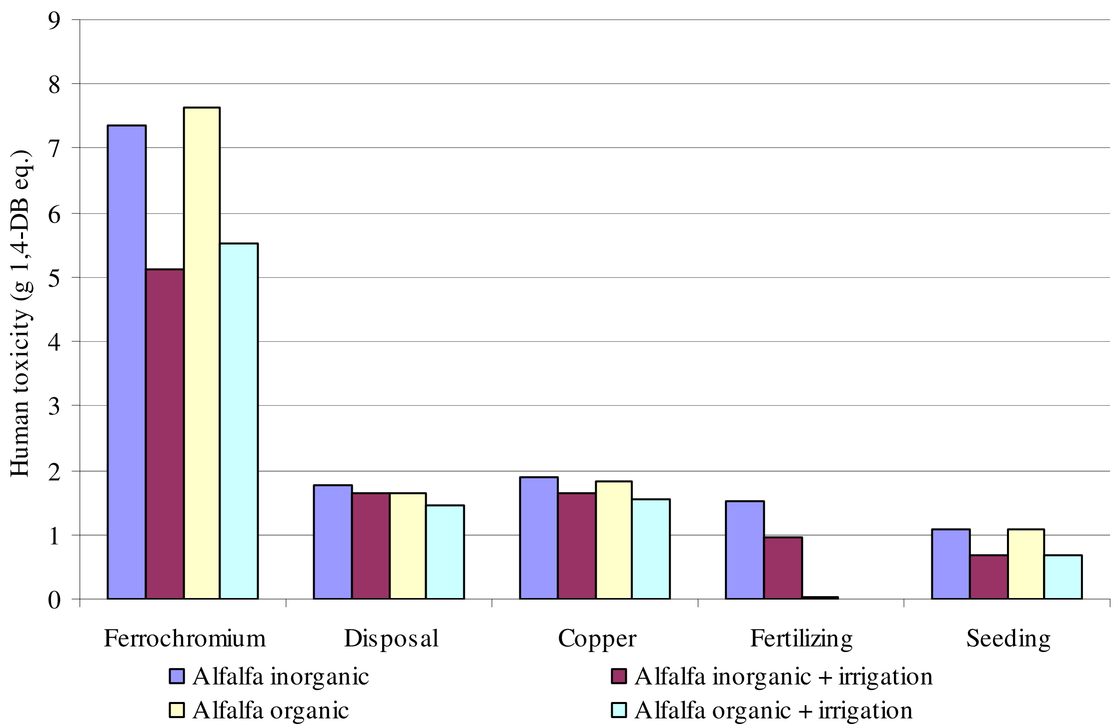


Figure 4.11: Process contribution at 5% cut-off for human toxicity (kg 1,4-DB eq) under different scenarios in the alfalfa cultivation subsystem (S1).

4.3.2 Environmental impact performance of baling and pre-processing subsystem (S2)

This subsystem had four scenarios which were associated with different input combinations used in S1. The inputs for baling and pre-processing differed according to the output produced from scenarios in S1. The performance of alfalfa produced using four different input combinations in S1 was taken into account in generating the environmental performance results under the four scenarios in S2. Appendix Table A.2 summarizes the LCA characterization results per 1 kg of alfalfa stem processed in S2. Similar to the results in S1, the overall results demonstrated no significant differences for AD, A, E and HT. However, major variation exits in GW for all four scenarios.

4.3.2.1 Abiotic depletion

How much of the natural resources such as coal, oil, phosphate, natural gas, uranium, bauxite, and iron are consumed by a system are represented by AD. Similar to S1, higher AD results were found in organic scenarios, while the inorganic scenarios had comparatively lower contributions to AD. The scenario with organic fertilizer showed a higher environmental burden due to additional agricultural machinery demands. Even though, irrigation required the use of extra machinery and energy, irrigated scenarios showed lower environmental burdens compared to non-irrigated scenarios due to the fact discussed in 4.3.1.1. Similar to S1, the scenario with inorganic fertilizer with irrigation seemed to be the best combination in S2.

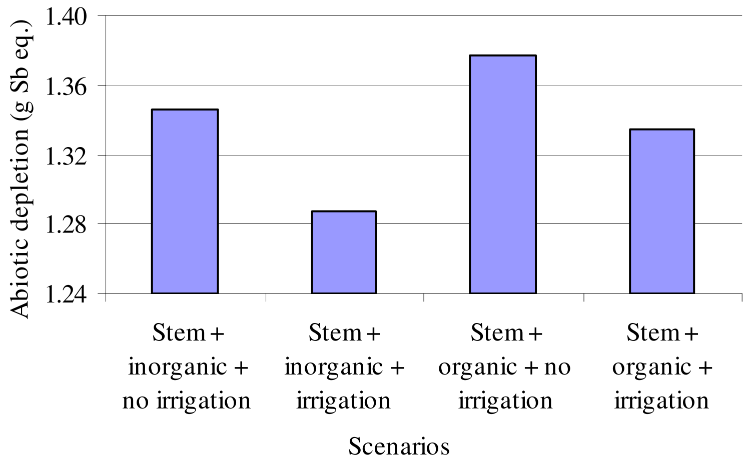


Figure 4.12: LCA characterization results for abiotic depletion based on 1 kg of alfalfa stem processed (including S1 and S2) for different scenarios.

Kadam (2002) reported that bagasse burning had a higher resource depletion index compared to E10 use since bagasse burning was driven by gasoline production while during ethanol production, lignin residue led to electricity offsets in E10.

4.3.2.2 Acidification

Acidification is caused by the emission of acidifying pollutants such as SO_2 and N_2O into the environment. As Figure 4.13 depicts, LCA results for acidification were similar to the results obtained in S1. Acidification was greater in organic scenarios than in inorganic scenarios, again reflecting higher machinery consumption and massive organic fertilizer application. In fact, the inorganic scenario with irrigation showed the least environment burden in terms of acidification.

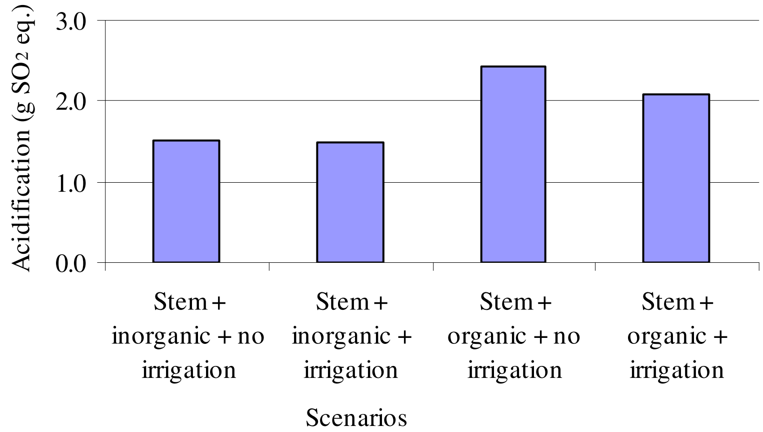


Figure 4.13: LCA characterization results for acidification based on 1 kg of alfalfa stem processed (including S1 and S2) for different scenarios.

Figure 4.14 shows the element contribution for acidification in each scenario. The elements those could contribute more than 5% to acidification were included there. It was apparent that ammonia was the main contributor for acidification in all four scenarios, whereas the contribution of SO_2 was less.

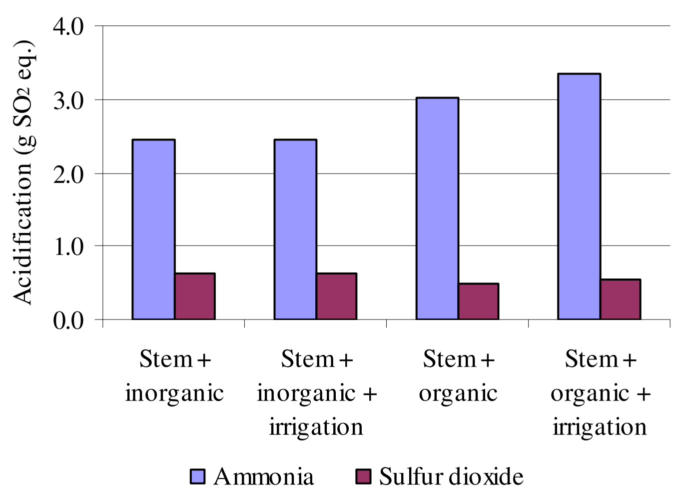


Figure 4.14: Inventory analysis for acidification for S2 at 5% cut-off.

4.3.2.3 Eutrophication

Similar to the results in S1 for eutrophication, inorganic scenarios showed higher eutrophication compared to organic scenarios (Figure 4.15).

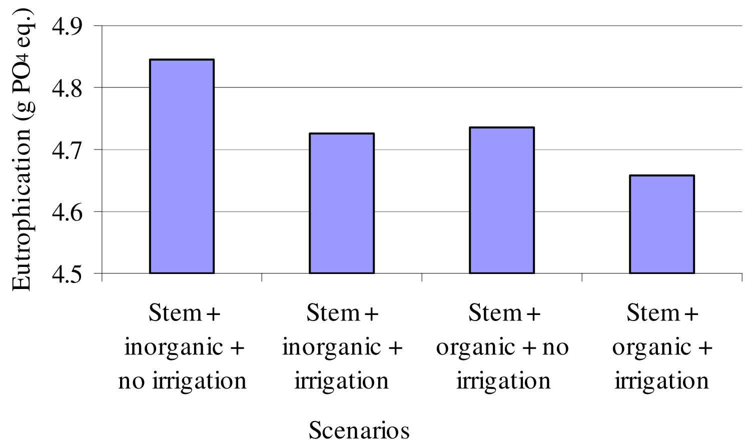


Figure 4.15: LCA characterization results for eutrophication based on 1 kg of alfalfa stem processed (including S1 and S2) for different scenarios.

In this case, the scenario with organic fertilizer and irrigation showed the least burden on the environment. Eutrophication results from high concentrations of macronutrients (such as N and P) in the environment. Irrigation reduces fertilizer concentration in irrigated scenarios.

4.3.2.4 Global warming potential

Figure 4.16 illustrates the significance of inorganic and organic scenarios in terms of global warming.

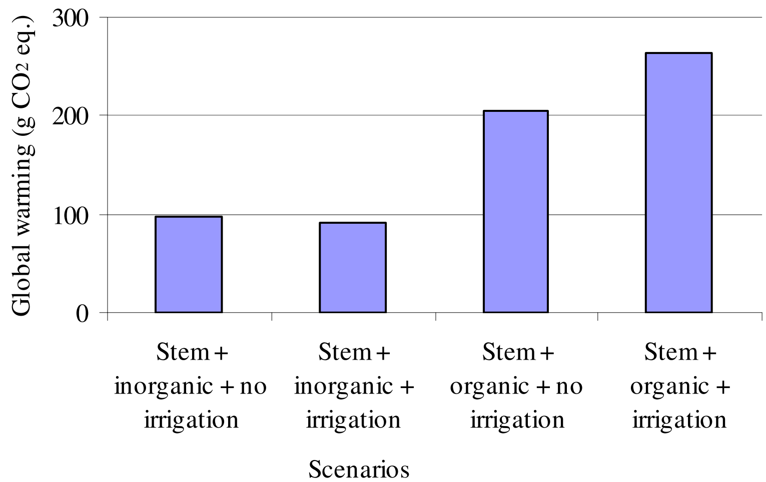


Figure 4.16: LCA characterization results for global warming based on 1 kg of alfalfa stem processed (including S1 and S2) for different scenarios.

Apparently, inorganic scenarios show lower environmental burdens while the organic scenarios show very high environmental burden. Similar to the results in S1 for GW, greenhouse gases are carbon dioxide, dinitrogen monoxide, and methane. Carbon dioxide emission is from fossil fuel used in S1 and S2 subsystems; it is emitted primarily from agricultural machinery operations. Kadam (2002) also reported that higher fossil energy use leads to higher fossil CO_2 emissions, resulting in higher GW impact. When organic fertilizer is used, the emission of methane is also significantly high, which contributes to higher global warming. Inorganic fertilizer with irrigation provided the lowest impact; hence, it is the most favourable input combination.

4.3.2.5 Human toxicity

The results show that irrigated scenarios showed lower burden in terms of HT. Toxic substances that affect human health were emitted largely during machinery production, as they were associated with emitted metal substances. Basically, chromium, copper, and nickel are emitted to the air and barite, barium, and selenium are emitted to water from machinery production, adversely affecting human health. The results in Figure 4.17 illustrate higher burdens in non-irrigated scenarios compared to those in irrigated scenarios; this situation is caused by the factors noted above. However, higher yield compensate part of the effect on irrigated lands.

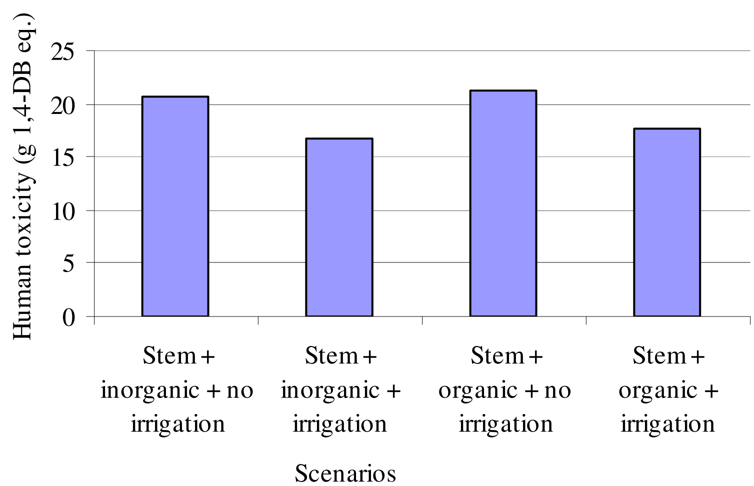


Figure 4.17: LCA characterization results for human toxicity based on 1 kg of alfalfa stem processed (including S1 and S2) for different scenarios.

4.2.3 Environmental impact performance of ethanol production subsystem (S3)

Analysis of this subsystem provided a cradle-to-gate life cycle analysis of environmental impacts associated with producing an alfalfa stem based bioethanol. This subsystem also followed the same scenarios as in S1 because the product of the first subsystem was an input into the next subsystem. Furthermore, in order to determine water recycling effects during the ethanol production process, 50% and 70% water recycling were considered separately in the subsystem (S3).

Therefore, this subsystem consisted mainly of following principal scenarios:

i) organic + irrigated + 50% water recycling

ii) organic + non-irrigated + 50% water recycling

iii) inorganic + irrigated + 50% water recycling

iv) inorganic + non-irrigated + 50% water recycling

v) organic + irrigated + 70% water recycling

vi) organic + non-irrigated + 70% water recycling

vii) inorganic + irrigated + 70% water recycling

viii) inorganic + non-irrigated + 70% water recycling

Tables 4.10 and 4.11 show the characterization results with, respectively, 50% water recycling and 70% water recycling under different scenarios.

Table 4.10: LCA characterization results for the impact categories based on 1 kg of ethanol production (total of S1, S2, and S3) under different scenarios at 50% water recycling.

Impact category	Ethanol + inorganic	Ethanol + inorganic + irrigation	Ethanol + organic	Ethanol + organic + irrigation
Abiotic depletion (g Sb eq.)	6.57	6.51	6.66	6.62
Acidification (g SO_2 eq.)	-10.71	-10.73	-9.87	-10.10
Eutrophication (g PO_4^{-3} eq.)	2.92	2.01	1.91	1.88
Global warming (g CO_2 eq.)	606.51	612.41	780.31	730.57
Human toxicity (g 1,4-DB eq.)	43.12	40.84	51.16	42.89

Table 4.11: LCA characterization results for the impact categories based on 1 kg of ethanol production (total of S1, S2, and S3) under different scenarios at 70% water recycling.

Impact category	Ethanol + inorganic	Ethanol + inorganic + irrigation	Ethanol + organic	Ethanol + organic + irrigation
Abiotic depletion (kg Sb eq)	6.90	6.76	6.99	6.87
Acidification (kg SO_2 eq)	-10.79	-10.82	-10.15	-10.43
Eutrophication (g PO_4^{-3} eq)	2.96	2.08	2.00	1.88
Global warming (g CO_2 eq)	645.08	626.21	792.19	744.37
Human toxicity (g 1,4-DB eq)	46.79	44.21	53.23	45.03

The results for both 50% and 70% water recycling cases had a similar pattern, but the magnitudes of the impacts were somewhat higher in scenarios with 70% water recycling. According to the results, global warming showed the highest environmental burden associated with the given four different scenarios, and the other impact categories had very low impacts. Evidently, GW is higher in 70% water recycling than in 50% water recycling scenarios due to additional energy consumption. As well, GW values for organic scenarios were greater than for inorganic scenarios because additional machinery was employed for organic production. In fact, an inorganic scenario with irrigation showed the lowest GW similar to S1 and S2 subsystems. Since the GW increased with increased water recycling, a 50% water recycling level was better than a 70% level. Previous studies demonstrated that a lignocellulosic biorefinery system producing bioethanol from wood residues could save up to 60% GHG emissions compared to those of fossil fuels (Cherubini et al. 2009).

The results for abiotic depletion did not show significant difference throughout all scenarios in Tables 4.10 and 4.11. However, non-irrigated scenarios had lower environmental burden compared to the irrigated scenarios.

There were environmental benefits associated with acidification in both 50% and 70% water recycling scenarios. These benefits could result from accounting for byproduct pathways such as protein and fibre components, which would have a positive impact on the whole system. Unlike S1 and S2, acidification impact showed higher environmental benefit in inorganic scenarios for both water recycling stages. Further, the irrigated scenarios showed comparatively higher environmental benefits than the non-irrigated scenarios.

Similar to the results in S1 and S2, eutrophication impact was varied slightly along the different scenarios, and it showed lower environmental burdens in scenarios with irrigation. Irrigation helped by diluting high concentrations of macronutrients in the environment, thereby reducing eutrophication effects better than non-irrigated conditions.

For instance, if inorganic fertilizers are used, they have to be applied with irrigation for lower eutrophication results. In the case of organic fertilizer application, the environmental burden was reduced with the application of irrigated water. Eutrophication was the lowest for organic irrigated scenario as given in both Tables 4.10 and 4.11, because the nutrient release from organic fertilizer was very slow as compared to inorganic fertilizer.

In both S1 and S2, human toxicity (HT) was higher in non-irrigated scenarios compared to irrigated scenarios. The magnitude of the effect was higher in scenarios with 70% water recycling relative to scenarios with 50% water recycling because additional energy was employed in the recycling process. Inventory analysis of human toxicity suggested that HT occurred chiefly from yeast production, alfalfa cultivation, processing, and heating processes in the ethanol plant. The key substance associated with HT is polycyclic aromatic hydrocarbons. In addition, barite, lead selenium, and barium elements contribute slightly.

Overall, it was apparent that the scenario with inorganic and irrigated conditions was the better combination for the ethanol production system (best case scenario) while, the scenario with organic fertilizer, non-irrigation, and 70%water recycling was the worst case scenario in this study. Referring to Tables 4.10 and 4.11, scenario with most favourable input combinations (i.e., inorganic fertilizers and with irrigation) was examined further to depict the effect of water recycling. Since there were marginal differences for AD, A, E and HT, only the results for GW were further analysed. Table 4.12 depicts results for inventory analysis of two scenarios: 50% and 70% water recycling.

Table 4.12: Inventory analysis of 50 % and 70 % water recycling scenarios.

Substance	Ethanol 50 % + inorganic (kg CO_2 eq.)	Ethanol 70 % + inorganic (kg CO_2 eq.)
Carbon dioxide	0.1342	0.1342
Carbon dioxide, fossil	0.9276	0.9597
Dinitrogen monoxide	-0.2856	-0.2838
Methane, fossil	0.0587	0.0618

Evidently, CO_2 and methane from fossil fuel were higher for 70% water recycling, as it required an additional amount of energy which caused higher environmental burdens in terms of GW. In fact, 70% water recycling has reduced the environmental benefit associated with dinitrogen monoxide compared to the results from 50% water recycling. It was apparent that the main cause for global warming in ethanol production came from carbon dioxide produced from fossil fuels. Fossil fuel was being used in farm machinery and other equipment operation from alfalfa cultivation to ethanol production. Applying remedies to minimize the use of fossil fuel will lead to a lower global warming impact.

In each subsystem (S1, S2, and S3), an inorganic irrigated scenario seemed to be the better coordination in terms of given impact categories. Therefore, comparison of three subsystems was carried out using the three scenarios. Figure 4.18 depicts the performance of S1, S2, and S3 under each impact category. According to the results, GW was the most influential impact category for all three subsystems. It increased with the increase in the number of processes in each subsystem. Therefore, S3 has the highest GW impact in ethanol production. Human toxicity also showed considerable impact in three subsystems, and it was highest at the S3.

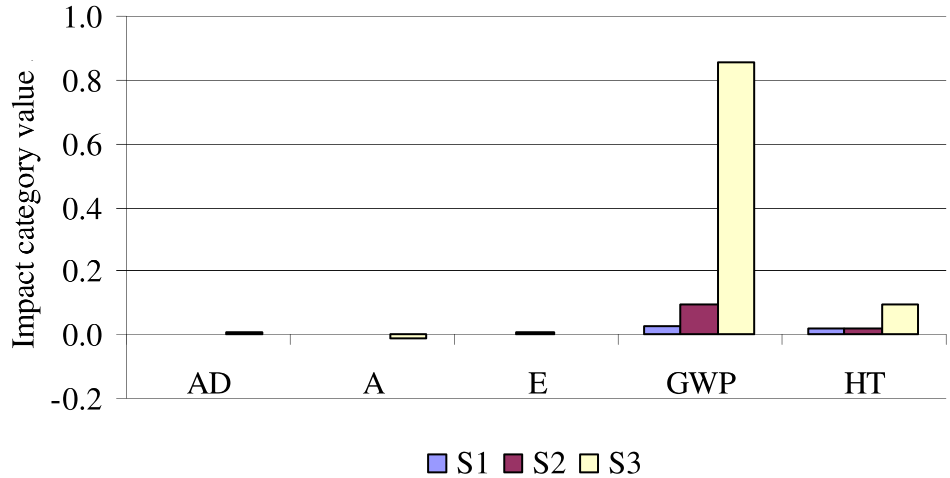


Figure 4.18: Comparison of S1, S2, and S3 for best case scenario in each system. Where S1: alfalfa cultivation subsystem, S2: baling and pre-processing subsystem, S3: ethanol conversion subsystem, AD: abiotic depletion, A: acidification, E: eutrophication, GWP: global warming potential, and HT: human toxicity.

4.2.4 Sensitivity analysis

Sensitivity analysis is an estimation of the effects of variations in the key parameters on the outcome. It is performed to investigate the influence of given parameters on the final result and helps to establish a degree of confidence in the results relative to the overall goal. The energy input into an ethanol production subsystem was the most important assumption during and at the end of the LCA since it was based on the cumulative value of total energy spent in the plant. Kemppainen and Shonnard (2005) also reported that process heaters were the largest energy consuming units in biomass-to-ethanol processes. Therefore, it is important to understand the impact of the input data on the final output results.

Detailed analysis of ethanol production subsystem (as given in Figure 4.19) shows the contribution of each process to the given impact categories. It was apparent that heat, enzyme, and yeast production have substantial involvement in AD, GW, and HT. Since enzyme and yeast production were excluded from the study, only heating processes were further analysed. Therefore, sensitivity analysis was performed using ten literature values for ethanol production with the minimum value of 9.5 MJ/L (Luo et al. 2009b) and maximum value of 21.3 MJ/L (Eggeman and Elander 2005) as given in Table 3.4 in section 3.3.3.4.

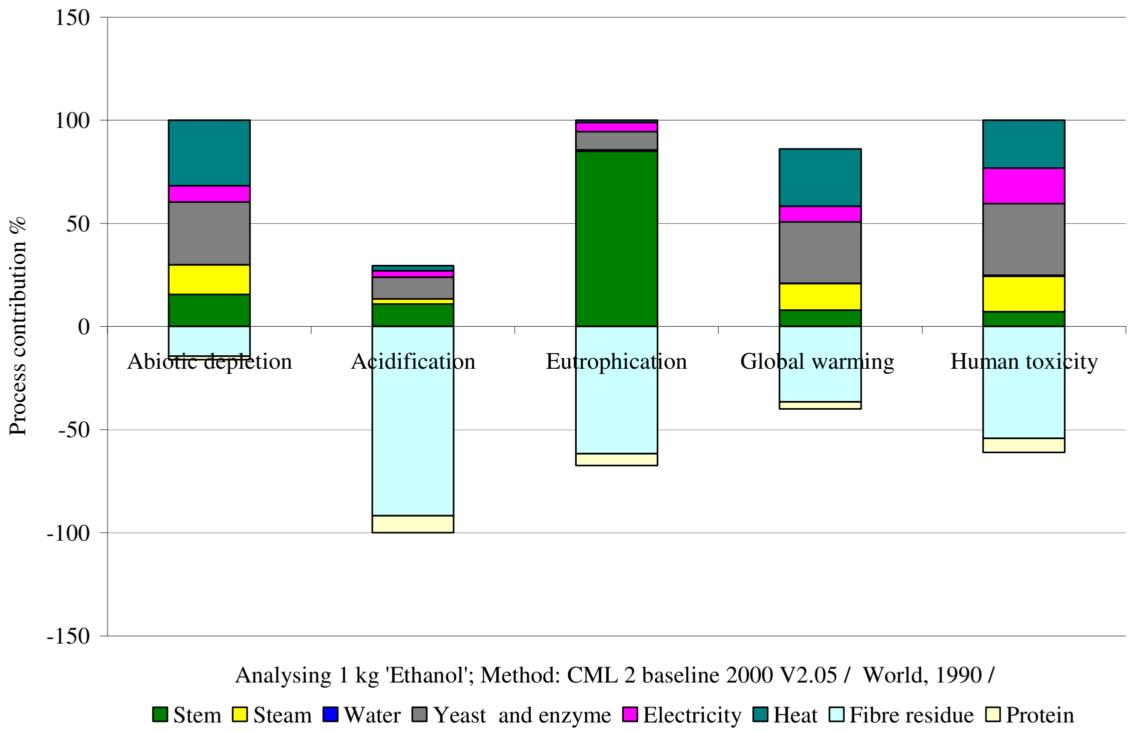


Figure 4.19: Process contribution to each impact category when producing 1 kg of ethanol (from total of S1, S2, and S3).

Figures 4.20 to 4.24 show the results of sensitivity analysis for given impact categories with the change in energy input. Error bars in each graph portray the variability in the results from the given energy values. For the given minimum and maximum energy values, the LCA results lie within the range of these error bars for each scenario. Error bars represent the maximum and minimum values of each population and the average values were represented by the bar charts.

According to the results in sensitivity analysis, the change in ethanol plant heat values had significant effects on AD over other impact categories. The abiotic depletion impact had a maximum range between 7.04 and 7.14 g Sb equivalent and minimum range between 5.34 and 5.44 g Sb equivalent. LCA results for S3 on AD were in this range.

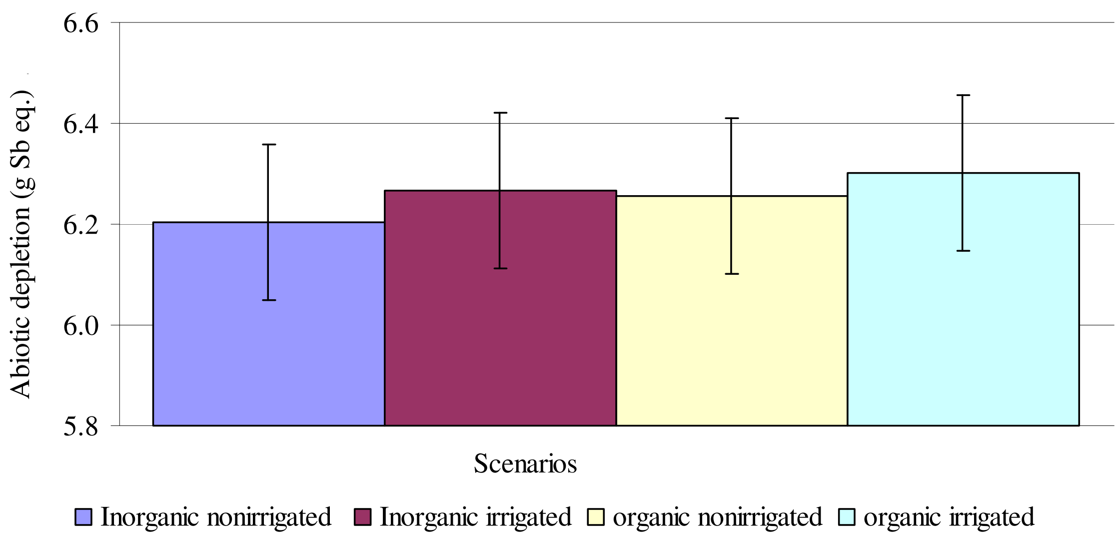


Figure 4.20: Sensitivity of abiotic depletion to the energy input (from total of S1, S2, and S3).

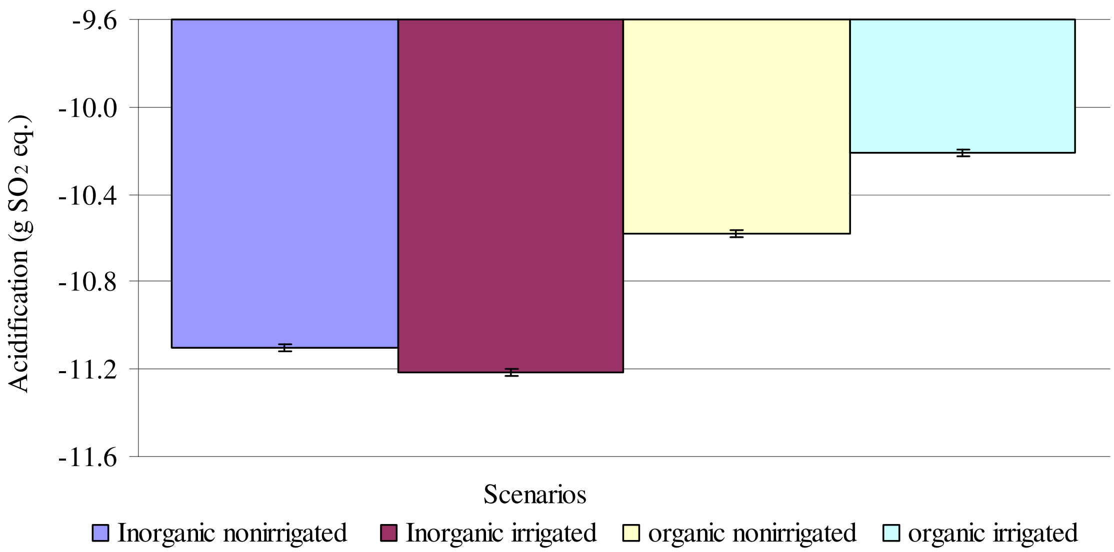


Figure 4.21: Sensitivity of acidification to the energy input (from total of S1, S2, and S3).

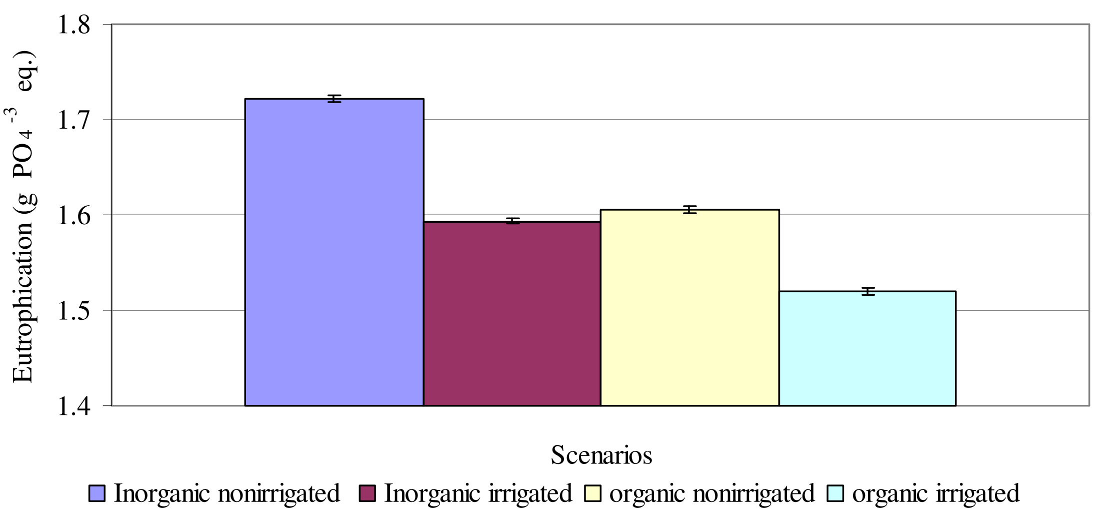


Figure 4.22: Sensitivity of eutrophication to the energy input (from total of S1, S2, and S3).

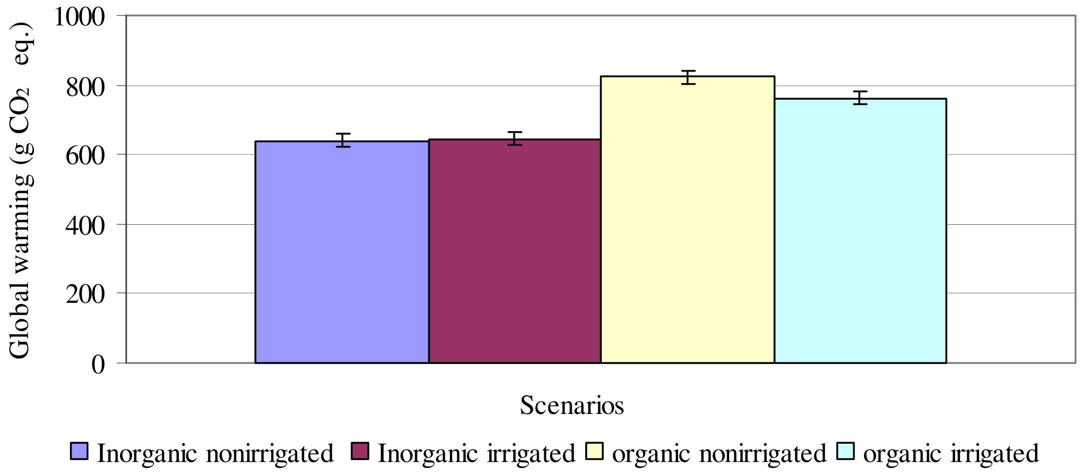


Figure 4.23: Sensitivity of global warming to the energy input (from total of S1, S2, and S3).

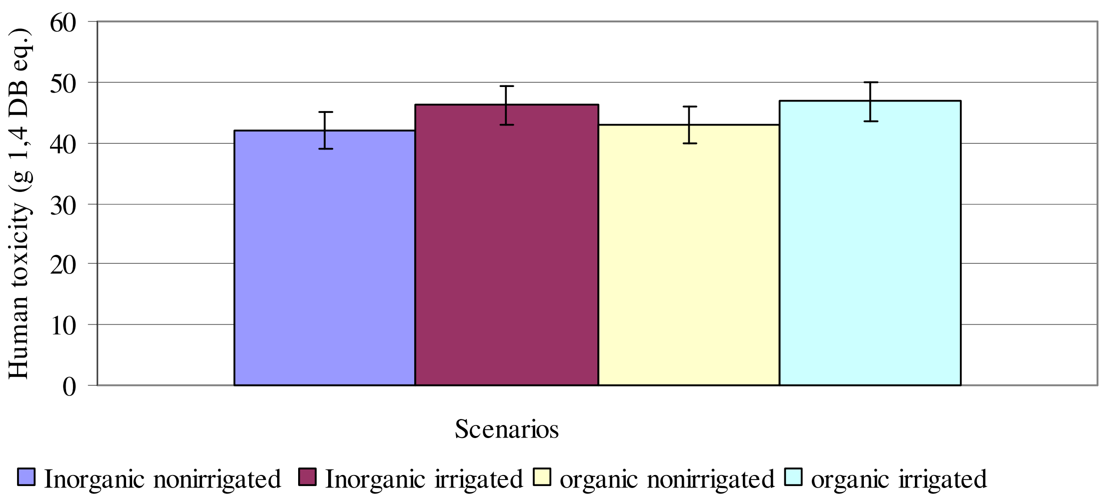


Figure 4.24: Sensitivity of human toxicity to the energy input (from total of S1, S2, and S3).

5. Conclusions and Recommendations

This chapter wraps up with a final discussion of life cycle results providing appropriate recommendations. The conclusions are associated with each subsystem and with ethanol production process as a whole (cradle-to-gate). The recommendations will include further modification of the study for more reliable output.

5.1 Summary and conclusions

The ethanol production process from alfalfa stem biomass was subdivided into three main subsystems, namely a cultivation subsystem (S1), a baling and pre-processing subsystem (S2), and an ethanol production subsystem (S3). Each subsystem was assessed in terms of energy utilization and environmental impacts. Additionally, material flow was calculated for the ethanol production subsystem. The following conclusions could be drawn from this study as a whole.

Investigation of alfalfa cultivation, logistics, and processing with emphasis on input use and energy consumption provide quantification of each input utilization and energy consumption in different subsystems.

Energy analysis of S1 shows that energy requirements for producing 1 kg of alfalfa under non-irrigated conditions range from 0.63 MJ to 1.30 MJ; for irrigated cultivation, the range is from 0.51 MJ to 0.94 MJ. The highest energy input was obtained by using organic fertilizer in alfalfa establishment. The use of inorganic fertilizer with irrigation is the best input combination in S1; it required 0.51 MJ/kg of energy.

Energy analysis of S2 shows that energy consumption for post harvest processing of 1 kg of alfalfa biomass ranges from 0.82 MJ to 1.62 MJ under different scenarios. The highest energy consuming process in S2 is drum drying, which takes 0.197 MJ/kg of electricity and heat.

Considering both S1 and S2, irrigated scenarios displays lower energy demand over non-irrigated scenarios; inorganic scenarios show lower energy demand over organic scenarios. Therefore, the most favourable scenario is inorganic irrigated condition in both subsystems.

Energy analysis of S3 for best case scenario shows that on average, 28.05 MJ to 38.43 MJ of energy is required to produce 1 L of ethanol excluding all the processes that biomass undergoes prior to being received at the ethanol plant. The average overall life cycle energy (from S1, S2, and S3) to produce 1 L of ethanol ranged from 36.65 MJ to 42.35 MJ. Similar to S1 and S2, inorganic irrigated scenarios have lower energy demands compared to those of the organic irrigated scenarios. The highest energy demanding process in S3 is ethanol plant heat energy, which is a cumulative value for this study. Average ethanol plant heat energy can be given as a range from 2.79 MJ/kg to 3.21 MJ/kg for 50% and 70% water recycling scenarios.

Comparing 50% and 70% water recycling demonstrates that 50% water recycling scenarios require less energy. Overall, inorganic irrigated 50% water recycling is the best scenario for S3 in terms of energy demand, and ranged from 6.81 MJ/kg to 9.03 MJ/kg. Sensitivity analysis of S3 for ethanol plant heat does not show significant change in the final output.

Comparing the three systems per kg basis reveals that alfalfa production consumed around 6.2% to 15.1% of the total energy. The ethanol conversion subsystem is the highest energy consuming subsystem in this study, falling into the 77.5% to 94.8% range for different scenarios. Baling and pre-processing subsystem shows around 3.5 to 4.0% contributions to the total.

Mass balance approach in S3 shows that approximately 6 kg of alfalfa stem biomass is needed to produce 1 kg of ethanol. Conversion of 6 kg of stem biomass into ethanol generated 0.9 kg of CO_2, 0.6 kg of protein residue, and 3.9 kg of fibre residue.

The environmental analysis of the aforementioned subsystems (according to five impact categories and using SimaPro CML 2 baseline 2000 method) provides conclusions that correspond to the energy consumption of each subsystem or process. Conversely, the higher the energy demand, the higher the environmental impact, which is a direct correlation.

Global warming (GW) is the most influential impact category in all three subsystems, whereas abiotic depletion (AD), acidification (A), eutrophication (E), and human toxicity (HT) have comparatively lower impact on each subsystem. Two major agricultural operations contribute to GW: i) the use of machinery (e.g., for seeding and spraying) in inorganic scenarios; ii) the application of compost in organic scenarios.

Compared to the use of organic fertilizers, the application of inorganic fertilizers decreases the impact of AD, A, GW, and HT while slightly increases E. In addition, the magnitude of each impact diminishes in scenarios with irrigation. The lowest burden on environment in terms of eutrophication is found in the scenario with organic fertilizer and irrigation. Similar to the other impact categories, global warming increased with increases in water recycling because of additional energy consumption; thus, 50% water recycling is better than 70% water recycling.

Comparison of three subsystems in terms of given impact categories concludes that inorganic, non-irrigated scenario with 50% water recycling is the most favourable input combination corresponding to the results of life cycle analysis.

5.2 Recommendations

The production of biofuels provides greater environmental benefits than fossil fuels can offer. However, there are still considerable areas associated with biofuel production where improvements should be made in order to reduce the energy consumption of the entire biomass-to-ethanol production system. The results of the study were highly affected by input and output data and by the modeling methodology of LCA. Allocation is one of the crucial issues in this study. Alfalfa produces two outputs: leaves and stems. Each component has a significant impact on LCA. Even though mass allocation was adopted, the results would likely have a significant effect with the use of economic allocation. This study focused on five environmental impact categories: acidification, abiotic depletion, global warming, eutrophication, and human toxicity. However, to achieve a more complete perspective of their impact on ethanol production, further studies are necessary. The design of this study did not present an optimized design, since all the sub-processes of ethanol production subsystems could not be added separately. Future research could also study alfalfa biomass densification, including its role in offsetting GHG emissions and improving the overall energy balance of an alfalfa-based ethanol biorefinery.

The work represented here, however, can serve as a model for a Canadian based cellulosic biorefinery. Such a biorefinery has the potential to elaborate major ethanol output and co-product credits with an integrated feedlot facility. Sustainability and efficiency can be incorporated into industries that actualize what this research and subsequent investigations can envision.

GLOSSARY

Allocation	Partitioning the input or output flows of a process or other product system to the product system under study (International Organization for Standardization 14040).
Acidification	Acidification is caused by releases of protons in the terrestrial or aquatic ecosystems.
Abiotic depletion	Depletion of natural resources such as iron, crude oil, etc. is under consideration.
Eutrophication	A process where water bodies receive excess nutrients that stimulate excessive plant growth.
Ecoinvent	The Swiss centre for Life Cycle Inventories. It is responsible for extending, updating, and preserving the high quality of the Ecoinvent 2000 database.
Functional unit	Quantified performance of a product system for use as a reference unit (International Organization for Standardization 14040).
Global warming	Climate change that causes an increase in the average temperature of the lower atmosphere.
Human toxicity	Characterization of toxic chemicals with relevance to human exposure primarily based on threshold limit values that are considered.
Life cycle	Consecutive and interlinked stages of a product system, from raw material acquisition or generation of natural resources to final disposal (International Organization for Standardization 14040).
Life Cycle Assessment	Compilation and evaluation of the inputs, outputs, and the potential environmental impacts of a product system throughout its life cycle (International Organization for Standardization 14040).
Life Cycle Impact Assessment	Phase of life cycle assessment aimed at understanding and evaluating the magnitude and significance of the potential environmental impacts of a product system (International Organization for Standardization 14040).

Life Cycle Inventory Analysis A phase of life cycle assessment involving the compilation and quantification of inputs and output, for a given product system throughout its life cycle (International Organization for Standardization 14040).

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APPENDIX A

Table A.1: LCA characterization results for the impact categories under study based on 1 kg of alfalfa cultivation (S1 only) using different scenarios.

Impact category	Unit	Alfalfa inorganic + no irrigation	Alfalfa inorganic + irrigation	Alfalfa organic + no irrigation	Alfalfa organic + irrigation
Abiotic depletion	g Sb equivalent	0. 23	0.17	0.26	0.21
Acidification	g SO_2 equivalent	0.26	0.25	1.18	0.84
Eutrophication	g PO_4^{-3} equivalent	0.39	0.28	0.29	0.21
Global warming	g CO_2 equivalent	29.27	23.81	195.44	138.49
Human toxicity	g 1,4-DB equivalent	25.62	21.72	26.15	22.55

Table A.2: LCA characterization results for the impact categories under study based on 1 kg of alfalfa stem biomass baling and pre-processing (S1 and S2), using different scenarios.

Impact category (kg Sb eq)	stem + inorganic	stem + inorganic + irrigation	stem + organic	stem + organic + irrigation
Abiotic depletion (g Sb eq)	1.35	1.29	1.38	1.33
Acidification (g SO_2 eq)	1.51	1.49	2.42	2.08
Eutrophication (g PO_4^{-3} eq)	4.84	4.73	4.74	4.66
Global warming (g CO_2 eq)	96.39	90.93	262.61	205.61
Human toxicity (g 1,4-DB eq)	20.66	16.76	21.18	17.58

Table A.3: Mass balance calculation for processing 1 kg of alfalfa stem feedstock at 50% water recycling.

Mass in	kg/h	Mass out	kg/h
Pretreatment			
Chopped alfalfa	1.00	Steam exploded substrate	1.63
Steam	0.63	Steam recycling	0.00
Total	1.63	Total	1.63
SSF			
Wash water after pretreatment	1.68	Ethanol from pentose	0.02
Water adjust at hydrolysis	4.37	Ethanol from hexose	0.14
*Recycle water	3.03	Total pure ethanol	0.16
*Add new water to adjust hydrolysis	1.34	CO_2 from pentose	0.02
Wash water after hydrolysis	1.02	CO_2 from hexose	0.14
Enzyme and yeast	0.33	Total CO_2	0.16
Steam exploded substrate	1.63	Acetic acid	0.00
		Glycerol	0.01
		Xylitol	0.01
		Solid residue + others	8.69
Total	9.03	Total	9.03
Distillation			
Fermented slurry	6.24	Ethanol (95%)	0.17
		Solid residue	2.63
		*Fibre residue	0.66
		Stillage	6.07
		*Protein residue	0.10
		*Waste water	4.91
		* Recycled water	3.03
Total	6.24	Total	6.24

Table A.4: Mass balance calculation for processing 1 kg of alfalfa stem feedstock at 70% water recycling.

Mass in	kg/h	Mass out	kg/h
Pretreatment			
Chopped alfalfa	1.00	Steam exploded substrate	1.63
Steam	0.63	Steam recycling	0.00
Total	1.63	Total	1.63
SSF			
Wash water after pretreatment	1.68	Ethanol from pentose	0.02
Water adjust at hydrolysis	4.37	Ethanol from hexose	0.14
*Recycle water	4.25	Total pure ethanol	0.16
*Add new water to adjust hydrolysis	0.12	CO_2 from pentose	0.02
Wash water after hydrolysis	1.02	CO_2 from hexose	0.14
Enzyme and yeast	0.33	Total CO_2	0.16
Steam exploded substrate	1.63	Acetic acid	0.00
		Glycerol	0.01
		Xylitol	0.01
		Solid residue + others	8.69
Total	9.03	Total	9.03
Distillation			
Fermented slurry	6.24	Ethanol (95%)	0.17
		Solid residue	2.63
		*Fibre residue	0.66
		Stillage	6.07
		*Protein residue	0.10
		*Waste water	3.70
		* Recycled water	4.25
Total	6.24	Total	6.24

Table A.5: Mass balance calculation for processing 1 L of ethanol produced at 50% water recycling.

Mass in	kg/h	Mass out	kg/h
Pretreatment			
Chopped alfalfa	4.69	Steam exploded substrate	7.64
Steam	2.95	Steam recycling	0.00
Total	7.64	Total	7.64
SSF			
Wash water after pretreatment	7.87	Ethanol from pentose	0.10
Water adjust at hydrolysis	20.48	Ethanol from hexose	0.66
*Recycle water	14.22	Total pure ethanol	0.76
*Add new water to adjust hydrolysis	6.26	CO_2 from pentose	0.10
Wash water after hydrolysis	4.78	CO_2 from hexose	0.64
Enzyme and yeast	1.55	Total CO_2	0.74
Steam exploded substrate	7.64	Acetic acid	0.02
		Glycerol	0.04
		Xylitol	0.04
		Solid residue + others	40.71
Total	42.31	Total	42.31
Distillation			
Fermented slurry	29.23	Ethanol (95%)	0.79
		Solid residue	12.34
		*Fibre residue	3.09
		Stillage	28.44
		*Protein residue	0.46
		*Waste water	23.02
		* Recycled water	14.22
Total	29.23	Total	29.23

Table A.6: Mass balance calculation for processing 1 L of ethanol produced at 70% water recycling.

Mass in	kg/h	Mass out	kg/h
Pretreatment			
Chopped alfalfa	4.69	Steam exploded substrate	7.64
Steam	2.95	Steam recycling	0.00
Total	7.64	Total	7.64
SSF			
Wash water after pretreatment	7.87	Ethanol from pentose	0.10
Water adjust at hydrolysis	20.48	Ethanol from hexose	0.66
*Recycle water	19.91	Total pure ethanol	0.76
*Add new water to adjust hydrolysis	0.57	CO_2 from pentose	0.10
Wash water after hydrolysis	4.78	CO_2 from hexose	0.64
Enzyme and yeast	1.55	Total CO_2	0.74
Steam exploded substrate	7.64	Acetic acid	0.02
		Glycerol	0.04
		Xylitol	0.04
		Solid residue + others	40.71
Total	42.31	Total	42.31
Distillation			
Fermented slurry	29.23	Ethanol (95%)	0.79
		Solid residue	12.34
		*Fibre residue	3.09
		Stillage	28.44
		*Protein residue	0.46
		*Waste water	17.33
		* Recycled water	19.91
Total	29.23	Total	29.23

APPENDIX B

Univariate Analysis of Variance for total energy values in Table 4.5.

Between-Subjects Factors

		N
Scenarios	S1 (Inorganic non-irrigated)	10
	S2 (Inorganic irrigated)	10
	S3 (Organic non-irrigated)	10
	S4 (Organic irrigated)	10

Tests of Between-Subjects Effects

Dependent Variable: Energy

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	3.803(a)	3	1.268	3.314	.031
Intercept	2659.30	1	2659.302	6952.35	.000
Scenarios	3.803	3	1.268	3.314	.031
Error	13.770	36	.383		
Total	2676.87	40			
Corrected Total	17.573	39			

a R Squared = .216 (Adjusted R Squared = .151)

Post Hoc Tests

Scenarios
Multiple Comparisons

Dependent Variable: Energy

	(I) Scenarios	(J) Scenarios	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
						Lower Bound	Upper Bound
Tukey HSD	S1	S2	.1136	.27659	.976	-.6313	.8585
		S3	-.6792	.27659	.085	-1.4242	.0657
		S4	-.3186	.27659	.660	-1.0635	.4263
	S2	S1	-.1136	.27659	.976	-.8585	.6313
		S3	-.7929(*)	.27659	.033	-1.5378	-.0480
		S4	-.4322	.27659	.412	-1.1771	.3127
	S3	S1	.6792	.27659	.085	-.0657	1.4242
		S2	.7929(*)	.27659	.033	.0480	1.5378
		S4	.3606	.27659	.567	-.3843	1.1056
	S4	S1	.3186	.27659	.660	-.4263	1.0635
		S2	.4322	.27659	.412	-.3127	1.1771
		S3	-.3606	.27659	.567	-1.1056	.3843
LSD	S1	S2	.1136	.27659	.684	-.4473	.6746
		S3	-.6792(*)	.27659	.019	-1.2402	-.1183
		S4	-.3186	.27659	.257	-.8795	.2423
	S2	S1	-.1136	.27659	.684	-.6746	.4473
		S3	-.7929(*)	.27659	.007	-1.3538	-.2319
		S4	-.4322	.27659	.127	-.9932	.1287
	S3	S1	.6792(*)	.27659	.019	.1183	1.2402
		S2	.7929(*)	.27659	.007	.2319	1.3538
		S4	.3606	.27659	.201	-.2003	.9216
	S4	S1	.3186	.27659	.257	-.2423	.8795
		S2	.4322	.27659	.127	-.1287	.9932
		S3	-.3606	.27659	.201	-.9216	.2003

Based on observed means.
* The mean difference is significant at the .05 level.

APPENDIX C

Univariate Analysis of Variance for total energy values in Table 4.6.

Between-Subjects Factors

		N
Scenarios	S1 (Inorganic non-irrigated)	10
	S2 (Inorganic irrigated)	10
	S3 (Organic non-irrigated)	10
	S4 (Organic irrigated)	10

Tests of Between-Subjects Effects

Dependent Variable: Energy

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	3.803(a)	3	1.268	2.506	.044
Intercept	2938.542	1	2938.542	5808.992	.000
Scenarios	3.803	3	1.268	2.506	.044
Error	18.211	36	.506		
Total	2960.556	40			
Corrected Total	22.014	39			

a R Squared = .173 (Adjusted R Squared = .104)

Post Hoc Tests

Scenarios

Multiple Comparisons

Dependent Variable: Energy

	(I) Scenarios	(J) Scenarios	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
						Lower Bound	Upper Bound
Tukey HSD	S1	S2	.1137	.31808	.984	-.7430	.9703
		S3	-.6792	.31808	.161	-1.5359	.1774
		S4	-.3186	.31808	.749	-1.1753	.5381
	S2	S1	-.1137	.31808	.984	-.9703	.7430
		S3	-.7929	.31808	.078	-1.6495	.0638
		S4	-.4323	.31808	.533	-1.2889	.4244
	S3	S1	.6792	.31808	.161	-.1774	1.5359
		S2	.7929	.31808	.078	-.0638	1.6495
		S4	.3606	.31808	.671	-.4960	1.2173
	S4	S1	.3186	.31808	.749	-.5381	1.1753
		S2	.4323	.31808	.533	-.4244	1.2889
		S3	-.3606	.31808	.671	-1.2173	.4960
LSD	S1	S2	.1137	.31808	.723	-.5314	.7588
		S3	-.6792(*)	.31808	.040	-1.3243	-.0341
		S4	-.3186	.31808	.323	-.9637	.3265
	S2	S1	-.1137	.31808	.723	-.7588	.5314
		S3	-.7929(*)	.31808	.017	-1.4380	-.1478
		S4	-.4323	.31808	.183	-1.0774	.2128
	S3	S1	.6792(*)	.31808	.040	.0341	1.3243
		S2	.7929(*)	.31808	.017	.1478	1.4380
		S4	.3606	.31808	.264	-.2845	1.0057
	S4	S1	.3186	.31808	.323	-.3265	.9637
		S2	.4323	.31808	.183	-.2128	1.0774
		S3	-.3606	.31808	.264	-1.0057	.2845

Based on observed means.
* The mean difference is significant at the .05 level.

APPENDIX D

Univariate Analysis of Variance for total energy values in Table 4.7.

Between-Subjects Factors

		N
Scenarios	S1 (Inorganic non-irrigated)	10
	S2 (Inorganic irrigated)	10
	S3 (Organic non-irrigated)	10
	S4 (Organic irrigated)	10

Tests of Between-Subjects Effects

Dependent Variable: Energy

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	123.700(a)	3	41.233	4.577	.008
Intercept	59758.157	1	59758.157	6632.69	.000
Scenarios	123.700	3	41.233	4.577	.008
Error	324.347	36	9.010		
Total	60206.204	40			
Corrected Total	448.047	39			

a R Squared = .276 (Adjusted R Squared = .216)

Post Hoc Tests

Scenarios

Multiple Comparisons

Dependent Variable: Energy

	(I) Scenarios	(J) Scenarios	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
						Lower Bound	Upper Bound
Tukey HSD	S1	S2	.5325	1.34236	.979	-3.0827	4.1478
		S3	-3.1827	1.34236	.101	-6.7979	.4326
		S4	-3.2773	1.34236	.087	-6.8926	.3380
	S2	S1	-.5325	1.34236	.979	-4.1478	3.0827
		S3	-3.7152(*)	1.34236	.042	-7.3305	-.0999
		S4	-3.8098(*)	1.34236	.036	-7.4251	-.1946
	S3	S1	3.1827	1.34236	.101	-.4326	6.7979
		S2	3.7152(*)	1.34236	.042	.0999	7.3305
		S4	-.0946	1.34236	1.000	-3.7099	3.5206
	S4	S1	3.2773	1.34236	.087	-.3380	6.8926
		S2	3.8098(*)	1.34236	.036	.1946	7.4251
		S3	.0946	1.34236	1.000	-3.5206	3.7099
LSD	S1	S2	.5325	1.34236	.694	-2.1899	3.2550
		S3	-3.1827(*)	1.34236	.023	-5.9051	-.4602
		S4	-3.2773(*)	1.34236	.020	-5.9997	-.5549
	S2	S1	-.5325	1.34236	.694	-3.2550	2.1899
		S3	-3.7152(*)	1.34236	.009	-6.4376	-.9928
		S4	-3.8098(*)	1.34236	.007	-6.5323	-1.0874
	S3	S1	3.1827(*)	1.34236	.023	.4602	5.9051
		S2	3.7152(*)	1.34236	.009	.9928	6.4376
		S4	-.0946	1.34236	.944	-2.8171	2.6278
	S4	S1	3.2773(*)	1.34236	.020	.5549	5.9997
		S2	3.8098(*)	1.34236	.007	1.0874	6.5323
		S3	.0946	1.34236	.944	-2.6278	2.8171

Based on observed means.
* The mean difference is significant at the .05 level.

APPENDIX E

Univariate Analysis of Variance for total energy values in Table 4.8.

Between-Subjects Factors

		N
Scenarios	S1 (Inorganic non-irrigated)	10
	S2 (Inorganic irrigated)	10
	S3 (Organic non-irrigated)	10
	S4 (Organic irrigated)	10

Tests of Between-Subjects Effects

Dependent Variable: Energy

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	322.357(a)	3	107.452	4.238	.012
Intercept	73655.560	1	73655.560	2905.05	.000
Scenarios	322.357	3	107.452	4.238	.012
Error	912.754	36	25.354		
Total	74890.670	40			
Corrected Total	1235.110	39			

a R Squared = .261 (Adjusted R Squared = .199)

Post Hoc Tests

Scenarios

Multiple Comparisons

Dependent Variable: Energy

	(I) Scenarios	(J) Scenarios	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
						Lower Bound	Upper Bound
Tukey HSD	S1	S2	6.0325	2.25186	.052	-.0322	12.0973
		S3	2.3173	2.25186	.734	-3.7474	8.3821
		S4	-1.4929	2.25186	.910	-7.5576	4.5719
	S2	S1	-6.0325	2.25186	.052	-12.0973	.0322
		S3	-3.7152	2.25186	.365	-9.7800	2.3496
		S4	-7.5254(*)	2.25186	.010	-13.5902	-1.4607
	S3	S1	-2.3173	2.25186	.734	-8.3821	3.7474
		S2	3.7152	2.25186	.365	-2.3496	9.7800
		S4	-3.8102	2.25186	.343	-9.8750	2.2545
	S4	S1	1.4929	2.25186	.910	-4.5719	7.5576
		S2	7.5254(*)	2.25186	.010	1.4607	13.5902
		S3	3.8102	2.25186	.343	-2.2545	9.8750
LSD	S1	S2	6.0325(*)	2.25186	.310	1.4656	10.5995
		S3	2.3173	2.25186	.031	-2.2496	6.8843
		S4	-1.4929	2.25186	.011	-6.0599	3.0741
	S2	S1	-6.0325(*)	2.25186	.108	-10.5995	-1.4656
		S3	-3.7152	2.25186	.007	-8.2822	.8518
		S4	-7.5254(*)	2.25186	.002	-12.0924	-2.9584
	S3	S1	-2.3173	2.25186	.031	-6.8843	2.2496
		S2	3.7152	2.25186	.007	-.8518	8.2822
		S4	-3.8102	2.25186	.099	-8.3772	.7568
	S4	S1	1.4929	2.25186	.031	-3.0741	6.0599
		S2	7.5254(*)	2.25186	.002	2.9584	12.0924
		S3	3.8102	2.25186	.099	-.7568	8.3772

Based on observed means.
* The mean difference is significant at the .05 level.